THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS

STUDIES ON ASPEN FIBERIZED CHIPS AND A CHLORINE DIOXIDE-ALKALI DELIGNIFICATION PROCESS

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COMPREHENSIVE REVIEW

Through the work described in Report Three it became apparent that holopulp of potential interest could be obtained by a process having three essential features. These are:

(i) fiberization of chips,

(ii) modification of lignin by an oxidant, and

(iii) removal of modified lignin by alkali.

The combination of the last two results in delignification, which is the most desirable reaction in chemical pulping.

The fiberization of chips was carried out under conditions aimed at achieving separations in the compound middle lamella region without undesirable chemical change, to provide whole individual fibers after delignification. Other processes such as those for making mechanical pulp or thermochemical pulp are less desirable because either too many fibers are broken and/or split or chemical changes such as excessive lignin condensation and carbohydrate hydrolysis occur. The conditions for fiberization of chips were selected without significant experimental study and based on:

(i) having a chip moisture content that would lead to fiberization at a high consistency,

(ii) raising the temperature of the moist chips rapidly to near boiling point to soften the lignin, especially in the region of the compound middle lamella, and

(iii) using a preheated double-disk refiner to fiberize the hot, moist chips as soon as possible after heating them.

The feasibility of achieving sufficient lignin modification with 9% chlorine dioxide as oxidant was also revealed through experiments reported in Report Three. In these, ambient temperatures were used at first, and the reaction times were about twenty hours at up to 3.0% consistency.

The removal of modified lignin by alkali was attempted in early experiments by extraction at 7.0% consistency with a total of 6% sodium hydroxide for one hour at 50°C. Although these conditions were selected without systematic experimental study, the results showed that appreciable delignification had occurred at a temperature low enough to expect good retention of the carbohydrates.

A 70%-yield pulp prepared at the point reached in Report Three had a markedly higher freeness and handsheets had about 50% greater opacity than had been recorded for pulps described in Report One.

When reviewing the investigations as outlined above, some questions that arose were:

1. Is there significant damage to chips during fiberization, or other evidence of room for improvement?

2. What kinds of modification are occurring in lignin through reaction with chlorine dioxide?

3. Can the amount of chlorine dioxide needed be significantly reduced?

4. Can gaseous chlorine dioxide be used instead of aqueous chlorine dioxide?

5. What are the best conditions for removing modified lignin?

6. When an answer is found to the former question, to what extent will the carbohydrates be significantly changed, if at all?

7. What can be done to reduce screen rejects and obtain individual fibers?

8. Can the pulps obtained be satisfactorily bleached without sacrifice of carbohydrate yield?

9. How versatile is a process based on the three essential features already named in terms of the types of pulp capable of being produced at a yield from 65% upward?

Understandably, opinions vary concerning which questions should be answered first. Report Four has already contributed much information to the second question, and the present report includes studies used for selecting conditions applied in concurrent work, covered by Report Five, on the use of gaseous chlorine dioxide.

In continuing the work of Report Three, consideration has been given to the first question. Since damage to wood is significant only if it results in a paper product with qualities inferior to those in which the treatment is omitted, damage should be viewed within the framework of the relevant process. This was done by comparing data from chlorite pulps produced from both fiberized and small aspen chips. The conclusion reached is that chip fiberization apparently is being achieved without excessive changes detrimental to such properties as tear and breaking length. However, zero-span breaking length decreased by about 5%, which is interpreted to mean there is a measurable amount of damage to individual fibers.

Later, microscopic examination of pulps produced by delignification of fiberized chips with 9% chlorine dioxide and alkali showed more lignin remained in the fibers not yet completely separated. In addition, some fibers had a relatively undamaged outer secondary wall to which the primary wall was sometimes still attached, some fibers had a relatively weak wall outside the main secondary wall, and others apparently had been damaged by compression. Evidence also indicated that the fiberized chips contain some aggregates of fibers large enough to restrain the removal by water of partially modified lignin through the existing porous structure. Thus, it is concluded that while considerable success has been achieved in meeting the objective of fiberization of chips, there is room for improvement in uniformity.

It is not obvious whether attention should be directed to reducing the amount of chlorine dioxide needed before studying the role of alkali in delignification. Since in any new pulping process the usefulness of the pulp has to be established, attention has been concentrated first on the role of alkali because this was felt to have greater potential than chlorine dioxide for causing significant changes in fiber properties.

Although experiments discussed in Report One appeared to reveal a three- to fourfold increase in carbohydrate removal when aspen was extracted with alkali prior to chlorite delignification, information in Reports Two and Three showed this effect is discounted when modified lignin analyses are taken into account. Results discussed in the present report are consistent with that finding. Thus, the indicated advantages of extracting with alkali before oxidation need to be considered. These include:

(i) increase in rate of delignification, and

(ii) increased separation of fibers in the compound middle lamella region.

For fiberized chips compared with shreds, through experiments with excess oxidant it has now been shown not only that the rate of reduction in Klason lignin is much faster, but also that the influence of alkali extraction before oxidation is diminished. This indicates that fiberized chips are reduced in size to such a desirable degree that benefit is obtained through the reaction with lignin being both greatly facilitated and less dependent on alkali extraction before oxidation. The experiments with excess oxidant also provide an indication that the extent to which the combined action of oxidant and alkali extraction leads to separation into individual fibers is related to yield.

To study the role of alkali on a more quantitative basis, exploratory experiments described in this report then established that a pulp can be made from fiberized chips at about 70% yield in three steps including a one-step reaction with 9% chlorine dioxide for about five hours at 5.0% consistency. This represents a significant improvement over the position reached in Report Three. At the same time, it was observed that unbleached pulps obtained by chlorine dioxide-alkali delignification had significantly fewer screen rejects when fiberized chips were first extracted with caustic. The more extensive handsheet data obtained on a pulp prepared by this route advanced the Report Three status of the project by demonstrating that, with beating, freeness, sheet density, and breaking length were reminiscent of a kraft pulp from the same chips.

After these exploratory experiments, fiberized chips were extracted with alkali and then reacted with 9.0% chlorine dioxide without varying the conditions to provide the material used to learn more about the role of alkali in the process. It is now known that:

(i) by raising the extraction temperature from 40 to 60°C., more rapid and complete removal of total modified lignin is favored,

(ii) by raising the extraction temperature from 40 to 60°C., there is no difference, detectable by sugar analyses, in the polysaccharides retained for a given extraction time,

(iii) by increasing the extraction time, there is a significant difference, detectable by sugar analyses, in the polysaccharides retained and this difference is independent of extraction temperature between 40 and 60°C.,

(iv) by increasing the extraction time, there is a difference in the papermaking properties of the unbleached fibers obtained, and

(v) by considering total yield, screen rejects, and screened yield, a fiber liberation point, which is independent of extraction time and temperature, was found to occur at about 70% total yield.

Some bleaching experiments have shown that while neither chlorine dioxide nor peroxide is satisfactory for increasing brightness, a single-stage bleach with hypochlorite raised the brightness to about 80 GE without sacrifice of carbohydrate yield. Hypochlorite bleaching aided separation into individual fibers and led to the unusual situation where the relatively unbeaten bleached pulp was more like the corresponding beaten unbleached pulp.

It is now clear that in chlorine dioxide-alkali delignification, alkali has a positive influence on fiber properties. Some indication of the extent to which process changes can significantly vary handsheet properties is being obtained to determine the potential versatility of this pulping process.

Future pulping work is expected to be concerned with:

(i) further reduction in the amount of chlorine dioxide needed, which will include consideration of its partial replacement by chlorine,

(ii) further consideration of other oxidants,

(iii) further increasing pulp brightness after bleaching,

(iv) further improvements through achieving better uniformity, such as in chip fiberization, and

(v) consideration of a softwood.

SUMMARY

Comparative experiments on the use of excess chlorite in the delignification of small hand-cut aspen chips and fiberized aspen chips showed that fiberization had no obvious adverse effect on potential holopulp yield. Decreasing the contact time between oxidant and fiberized chips seemed to lead to a pulp with both higher freeness and higher opacity. Chip fiberization apparently was achieved without excessive changes detrimental to some papermaking properties. Tear and opacity remained about unchanged, zero-span tensile strength decreased about 5%, while breaking length increased. Prior treatment of small aspen chips with 0.5$\underline{N}$ sodium hydroxide followed by reaction with excess chlorite was confirmed by photomicrographs to lead to greater fiber separation through increased cleavage in the compound middle lamella region.

Experiments on the reaction of fiberized chips, both with and without prior alkali extraction, with excess chlorite for a series of times again showed alkali extraction resulted in an apparent increase in carbohydrate removal. This arose from noncarbohydrate material that was removed by subsequent alkali extraction after which the yield differences linked to prior alkali extraction of chlorite-reacted pulps ceased to be significant. Data from the same experiments on fiberized chips showed that apparently the extent to which Klason lignin content is reduced is less dominated by the dimensions of the wood substance than when shreds were used previously. Thus, under similar reaction conditions, the former not only contained less Klason lignin but also showed less effect of caustic pretreatment on Klason lignin content. The relationships between yield, carbohydrates, and total modified lignin data plus visual examination of pulps disclosed that individual fibers are easily liberated at about 65 and 70% yield.

Preliminary experiments on the selective delignification of fiberized chips with 9.0% chlorine dioxide and different combinations of alkaline extractions are described. From these experiments there were selected the conditions used in a three-stage approach to preparing a holopulp made into handsheets for which similar data were obtained on a kraft pulp from the same lot of chips. The 70%-yield holopulp beat more easily to provide handsheets over about the same sheet density range as the kraft pulp. For both pulps the breaking length was similar at any given sheet density, zero-span breaking length was approximately 30% greater for the holopulp on an equal fiber-count basis, and the TAPPI tear factor of the two pulps was significantly different. The holopulp had a lower TAPPI tear factor for all except the lowest density handsheets.

The extractives removed from fiberized aspen chips by alkali were found to be capable of consuming up to about 0.7% chlorine dioxide on a fiberized chip basis.

Alkali-extracted fiberized aspen chips after reaction in water with 9.0% chlorine dioxide were extracted with about 6.0% sodium hydroxide for up to 8 hours at 40, 50, and 60°C., from which it was found that both time and temperature influence total yield and screen rejects. Three unbleached pulps prepared after alkali extraction at 50°C. for 10, 60, and 240 minutes, respectively, were made into handsheets. Less bulky sheets with fewer fiber bundles and higher breaking length were made as longer extraction time produced pulps from 73 to 68% yield. It was revealed that for a grab sample of chips, after reaction with 9% aqueous chlorine dioxide, alkali extraction for sufficient time at 40-60°C. led to fiber liberation at a 71-72% total yield.

The alkali extraction process was found to be not a simple first-order reaction. While the initial extraction rate approximately doubled for each 10°C. rise in temperature, at longer extraction times the rate is apparently less temperature dependent. Analytical data showed that it is the rate of removal of the acetone-soluble lignin portion of Buchanan's total modified lignin which is most influenced by raising the extraction temperature from 40 to 60°C. The higher temperature was shown to favor more rapid and more complete removal of total modified lignin, with fewer screen rejects, for a given extraction time. Consideration of the polysaccharides, through sugar analyses, indicated that changing the temperature from 40 to 60°C. had no effect at constant time. However, for 40 to 60°C., total detectable sugars decreased with longer extraction times without there being a similar decrease apparent in total modified lignin-free yield. This is interpreted to mean that extraction time causes changes in saccharide units without a parallel degree of solubilization. These observations were found to be applicable to either glucose or xylose, the main polysaccharide hydrolysis products.

Polyuronides and acetyl contents were found to decrease rapidly during the first part of the alkali extraction after reaction of fiberized chips with aqueous chlorine dioxide.

When considering the effect of increasing the extraction consistency from 8 to 12%, further fiber separation in a PFI mill resulted in about 3% of partially modified lignin being dissolved. Apparently, this material is not readily removed by water through the existing porous structure of fiberized chips after reaction with aqueous chlorine dioxide. Extraction at the highest consistency after further fiber separation resulted in the same degree of carbohydrate retention and a slightly lower level of lignin content that appears primarily associated with further fiberization rather than consistency change.

Exploratory bleaching experiments demonstrated that unbleached holopulps were not bleached to a high whiteness by either chlorine dioxide or peroxide. However, a single-stage bleach with hypochlorite raised the brightness to about 80 GE at about 65% yield. There is some evidence that time of extraction with alkali after reaction of fiberized chips with chlorine dioxide is a factor influencing pulp properties after bleaching. A mixture of pulps extracted with alkali for 60 minutes and for 240 minutes on bleaching with hypochlorite led to an unusual situation where the relatively unbeaten bleached pulp was more like the unbleached pulp after beating.

Photomicrographs are presented to show that bleaching with hypochlorite enhanced the degree of separation into individual fibers. However, studies of stained bleached fibers revealed that while most fibers were apparently delignified, lignin remained in some, especially those not yet completely separated into individual fibers. Unbeaten bleached fibers varied in their morphology. Some had a relatively weak wall outside the main secondary wall, whereas some had a relatively undamaged outer secondary wall to which the primary wall was sometimes still attached. Unbeaten, unbleached fibers were similarly heterogeneous, varied considerably in their ability to withstand swelling pressure and some showed evidence of compression damage that probably occurred during chip fiberization. Surface changes during alkali extraction of holocellulose fibers are discussed.

Oxidant consumption is discussed with a review of work in Report Four emphasizing lignin modification as a function of total chlorine dioxide added and the expectation of reducing chlorine dioxide requirement, possibly to 7.0%. Chlorine substitution during lignin modification by chlorine dioxide is also discussed as an indicated way to reduce the chlorine dioxide needed.

FIBERIZED VERSUS SMALL ASPEN CHIPS

DISCUSSION

Introductory Comment

In Report Three it was noted that the choice of fiberization conditions for chips is narrowed down to fitting between the situations where there is, on the one hand, mechanical damage and, on the other hand, undesirable chemical change. Both of these aspects of the fiberized aspen chips used in the exploratory studies were left to one side.

In considering whether the method used to fiberize aspen chips had possibly resulted in mechanical damage to individual fibers, it is apparent from the Bauer-McNett classification of pulps and photomicrographs, in Table X and Fig. 9-14 of Report Three, that many fibers had remained unbroken. If it is accepted for the time being that obvious mechanical damage was not extensive, it is relevant to compare more positively the papermaking potential of the chips before and after fiberization to check for the possibility of other undesirable change.

After some consideration, it was decided to use an approach of making a comparison by preparing holopulps both from chips reduced to about 1/8 in. in cross section by hand-cutting stock chips in the axial direction, and from fiberized chips. This would have the advantage of providing information on a basis closely related to that of envisaged experiments on delignification with chlorine dioxide as described later.

It had been learned already that chips about 1/8-in. square and 5/8-in. long are softened more readily by chlorite solution after prior treatment with alkali and that long exposure to the oxidant may be a factor in the pulp produced having a low freeness (Report Three, Table VIII). These facts were taken into account in planning the chlorite delignifications described in the experimental part, data on which are given in Tables I, II, and III.

Chlorite Holopulp Yields

In addition to preparing pulp from 1/8-in. by 5/8-in. chips (identified in Tables I, II, and III by the letters "B" and "C"), pulps from unscreened fiberized chips (identified by means of "D") and a screened fraction of fiberized chips ("E" and "F") were made. As can be seen from Table I, the unscreened fiberized chips are characterized by a lower yield obtained after reaction with chlorite. Although the explanation is uncertain, it appears there may have been excessive chemical reaction of the fraction passing a 28-mesh screen. Both the small chips and the screened fraction of fiberized chips gave about the same yield after reaction with chlorite and alkali. In a subsequent experiment, not described in this report, a product was obtained in 68.9 and 64.4% yield after reaction of unscreened fiberized aspen chips with chlorite and alkali, respectively, using the conditions applicable to F/II and F/III in Table I, which differed primarily in the shorter reaction with chlorite. Thus, it appears reasonable to conclude that fiberization of chips has no obvious adverse influence on potential holopulp yield when the degree of subdivision is allowed for by reducing the reaction time with chlorite.

Handsheet Data

From an examination of the Canadian freeness data in Table II it will be observed that Pulp C/III had an appreciably higher freeness than Pulps D/II, D/III, and E/III, all of which were reacted with chlorite for a similar time. By decreasing the time of reaction with chlorite to compensate for the higher degree of

TABLE I

CHLORITE-DELIGNIFIED PULPS FOR MAKING INTO HANDSHEETS[a]

Stage I (Pretreatment with alkali)

Pulp ref.	B/I	C/I	D/I	E/I	F/I

Stage II (Chlorite)

Pulp ref.	B/II	C/II	D/II	E/II	F/II
Time, hr.	24	24	24	29	16.5
Yield, %	71.6, 70.6	72.6	65.8,66.7	70.1	69.5

Stage III (Alkaline extraction)

Pulp ref.	B/III	C/III	D/III	E/III	F/III
Final pH	12.8	12.7	12.7	12.9	12.6
Yield, %	66.4	65.8	60.0	66.2	64.4
GE brightness	--	80	--	--	82

[a] A complete description of the materials and methods is given in the experimental part of this section.

TABLE II

BEATING CONDITIONS BEFORE PREPARING HANDSHEETS

Pulp	Valley Beater, total min./load	British Disintegrator, counts	Canadian Freeness, ml.
C/III	0	500	520
	5/0	600	460
	15/0	0	480
	22/1 kg.	600	365
	30/1 kg.	0	350
	33/1 kg.	600	290
	40/1 kg.	600	220
D/II	5/0	600	390
	15/0	600	340
	30/0	600	330
	35/1 kg.	600	270
	40/1 kg.	600	205
D/III	0	1500	250
	5/0	600	320
	15/0	600	310
	22/1 kg.	600	280
	26/1 kg.	600	240
	36/1 kg.	600	190
E/III	0	500	390
F/II	0	600	510
F/III	0	600	525
	14/1 kg.	600	425
	35/1 kg.	600	300
	55/1 kg.	600	190

TABLE III

HANDSHEET DATA

Pulp	Canadian Freeness	Density, g./cc.	Opacity, %	Breaking Length, m.	TAPPI Burst Factor	TAPPI Tear Factor	Zero-span Breaking Length, km.
C/III	460	0.705	68	7710	34	66	21.1
	365	0.726	68	7910	37	67	20.9
	290	0.739	67	8590	40	65	22.3
	220	0.755	66	9100	44	63	20.9
D/II	390	0.728	65	8510	48	68	17.3
	340	0.726	65	8820	51	68	17.7
	270	0.756	65	10,200	58	66	19.2
	205	0.780	63	10,600	61	63	20.4
D/III	250	0.751	69	9500	52	70	18.7
	320	0.726	69	8510	50	67	20.6
	280	0.735	68	9330	54	68	20.3
	240	0.772	68	9660	56	70	19.6
	190	0.785	64	10,000	60	68	20.4
E/III	390	0.741	69	8710	50	69	20.5
F/II	510	0.668	70	8100	40	70	18.9
F/III	525	0.700	71	7600	42	72	19.1
	425	0.713	67	8900	52	67	20.3
	300	0.772	68	10,200	59	65	19.9
	190	0.787	61	10,600	65	62	20.2

subdivision of the fiberized chips, it was found from Pulps F/II and F/III that small chips and fiberized chips were both capable of producing holopulps with a Canadian freeness of at least 500 ml. In addition, a previous indication that degree of exposure to oxidant has an influence on both freeness and opacity was confirmed. As is noted, for example, in Report Three, Table VIII on page 28, Pulp 4 obtained from small aspen chips after exposure to chlorite for 120 hr. had a Canadian freeness of 18 and a 61% opacity, whereas from Table III above it can be seen Pulps F/II and F/III had a 70-71% opacity.

Inspection of handsheet data in Table III reveals some obvious differences. The three pulps with lowest initial freeness, namely Pulps D/II, D/III, and E/III, all have comparatively higher sheet densities and breaking lengths than obtained for Pulps C/III and F/III. These differences are thought to be associated with the first group of pulps having a longer effective exposure time to chlorite. It is possible that inclusion of the fraction passing a 28-mesh screen in Pulps D/II and D/III might be regarded as significant when considering these differences. However, the tear and zero-span tensile properties for Pulp D/III compared with Pulp F/III (from which the through-28-mesh fraction was excluded) shows that exclusion of the through-28-mesh screen fraction had no influence on those properties. In considering the handsheet data in terms of fiberized versus small aspen chips, it appears appropriate for the comparison to be made between Pulps F/III and C/III.

Before making this comparison, the data for Pulps D/II and D/III will be considered since there are some differences related to the alkali extraction which appear noteworthy. For example, Pulp D/II was observed to be capable of being separated into individual fibers on beating as reflected by a parallel gain in zero-span tensile strength. In the unbeaten pulp, D/III, fiber separation was more complete and zero-span tensile strength remained essentially unchanged with beating. A second observation concerns the fact that the opacity data before, compared with after, alkali extraction show a change from lower to higher values, whereas in some experiments using aqueous chlorine dioxide the reverse change has been observed, as will be recorded later in this report.

From Table III and Fig. 1 a comparison of the data for Pulps F/III and C/III reveals that chip fiberization apparently was achieved without changes detrimental to some papermaking properties. Zero-span tensile strength shows a decrease of about 5%, tear and opacity remain about unchanged, while tensile strength as represented by breaking length has increased.

This is an interesting observation since the desirability of fiberizing wood before producing a chemical pulp has already been discussed by others (1), and Rydholm (2) has noted the unsatisfactory outcome of experiments already made to achieve this desire. It could be premature to claim on a broad basis that work already described here shows wood can be satisfactorily fiberized without damage prior to chemical delignification. Nevertheless, it has been pointed out previously (3) that damage to wood with reference to pulp quality is significant only if it results in a paper product with qualities inferior to those in which the treatment is omitted. In this sense, fiberized aspen chips, obtained as described in this project, appear to be desirable in producing a holopulp. At the same time, there is room for further consideration in this area, and some aspects of fiber morphology, for example, will be discussed later on.

Influence of Alkali on Chlorite Delignification of Chips

Reference was made above to the fact that small aspen chips are softened more readily by chlorite solution after prior treatment with alkali and, in Report

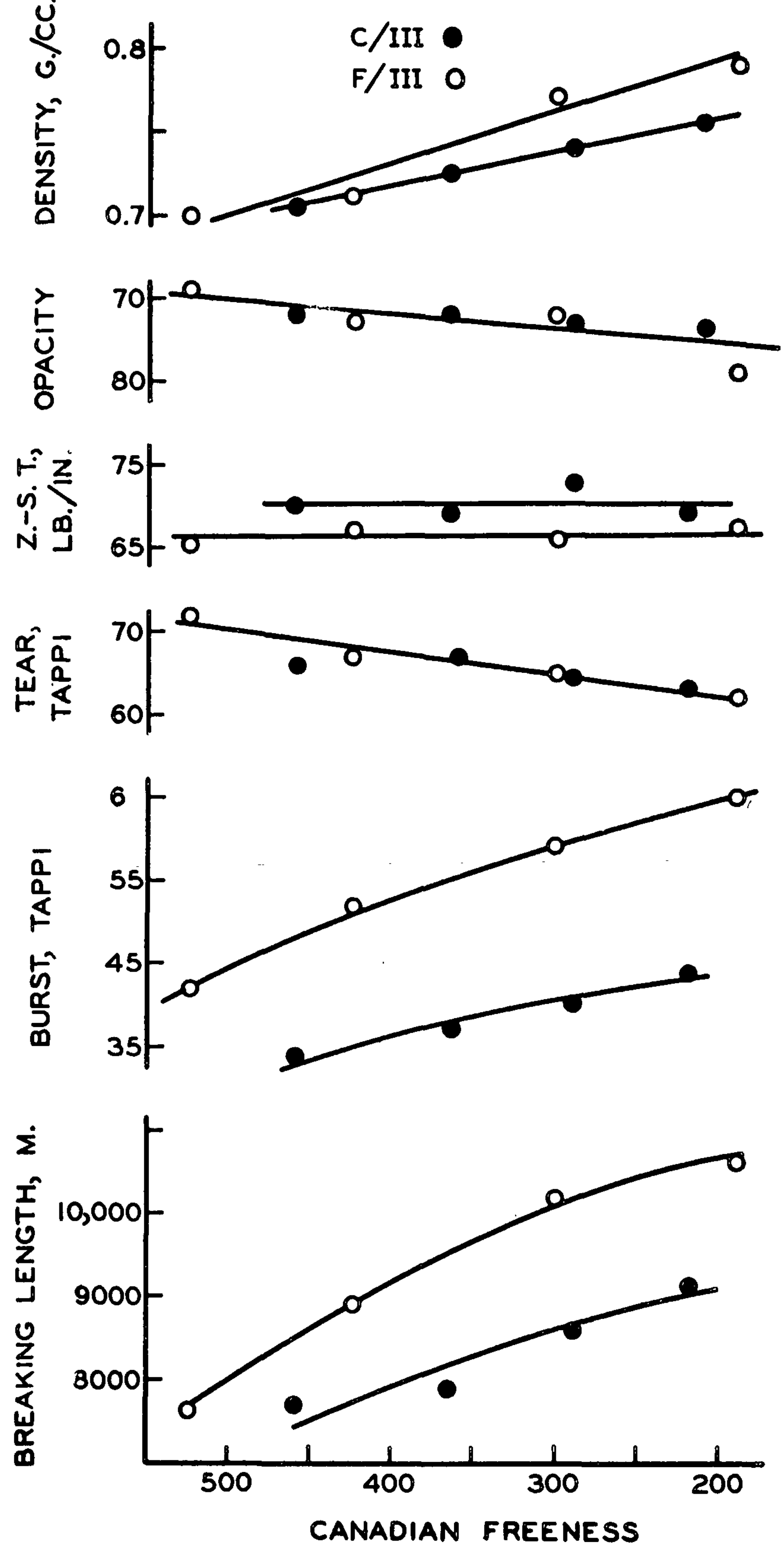

Figure 1. Comparison of Handsheet Data for Chlorite Holopulps from Handcut (C/III) and Fiberized Chips (F/III)

Three, Fig. 4 and 5 were presented to illustrate the extent to which fiber-to-fiber bonding had been influenced where reaction with chlorite was preceded by alkaline extraction. It was noted then that the cell wall structure was not accurately represented due to the method of preparation of the specimens. By employing a different technique, more satisfactory photomicrographs have now been obtained, as presented in Fig. 2 and 3. From these, it can be seen that prior treatment with 0.5N sodium hydroxide leads to considerable separation in the compound middle lamella region after reaction with chlorite, and the cell wall structure is more correctly represented without the induced swelling noted before. Differences in color after staining with Graff's "C" stain, for example, indicated the likely presence of more lignin-staining substance in the middle lamella region of the chips not pretreated with alkali.

EXPERIMENTAL

Raw Materials

The chips used were from the same lot as referred to in Report Three, page 55, and will be identified herein as Lot "A3/55."

Materials B, C, D, E, and F (Table I) from this lot of chips are described as follows:

B. Handcut chips about 1/8 in. in cross section and about 5/8 in. long.

C. Same as B.

D. Unscreened fiberized chips made using the conditions set out in Report Three, page 55, Table XIII.

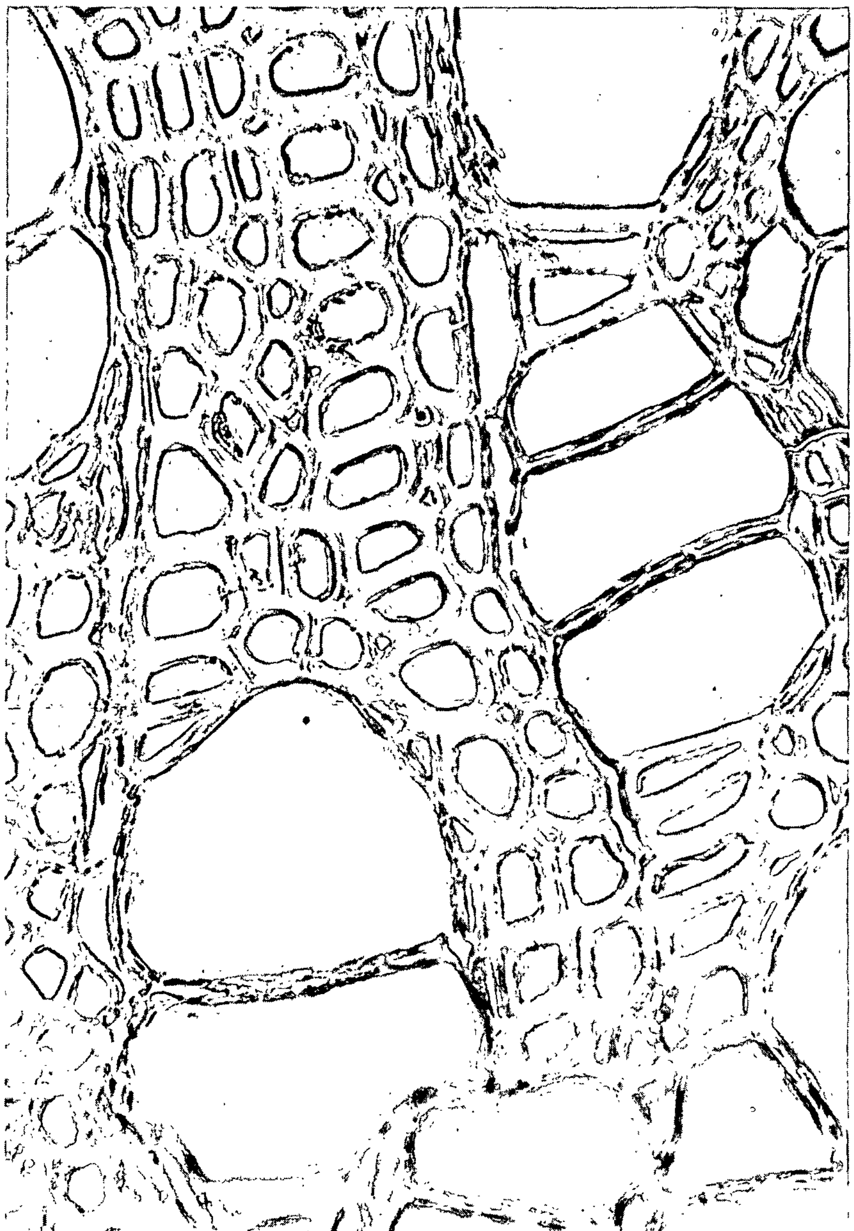

Figure 2. Cross Section of an Aspen Chip After Reaction with Chlorite, Showing Integrity of Structure. Sample Freeze Dried, Embedded in Butyl Methacrylate and Mounted in Mineral Oil; Magnification 750X

Figure 3. Cross Section of an Aspen Chip After Extraction with Alkali Followed by Reaction with Chlorite, Showing Separation in Compound Middle Lamella Region. Sample Freeze Dried, Embedded in Butyl Methacrylate and Mounted in Mineral Oil; Magnification 750X

E. Through-6-and-on-28-mesh Bauer-McNett fraction of fiberized chips prepared previously (see Report Three, page 55). The on-6-mesh, on-28-mesh, on-65-mesh, and on-150-mesh amounts were 196, 151, 70, and 24 g. (o.d.), respectively, in a typical classification.

F. Same as E.

Delignification and Disintegration

(Tables I and II.) The delignification experiments B, C, D, E, and F were carried out in three main steps described as follows.

Alkali pretreatment was carried out in a glass vessel with the chips (50 g. o.d.) covered by 500 ml. of 0.5N NaOH; then a vacuum was applied for 15 minutes at 25°C. before heating to 50°C. for 45 minutes, after which the extracted product was collected on a filter, washed with water several times, soaked in water 1 to 2 hours, filtered, covered with 9% aqueous acetic acid for 1-2 hours, filtered, and washed. Tests showed the interior of hand-cut chips to be acid to litmus.

Chlorite reaction was conducted by adding a volume of solution containing 10% aqueous sodium chlorite and 1.5% acetic acid to provide 100% $NaClO_2$ on an ovendry wood basis. The shaken reaction mixture was left at room temperature for the times recorded in Table I, and the temperature was observed to rise to 32°C. in the early part of the oxidation. After reaction for the time shown, the products were collected on sintered-glass funnels, washed with several changes of water, covered with water for about 1 hour, filtered, and the yields determined (see Table I). Samples of chips were fiberized for yield determinations.

Alkali extraction was carried out at ambient temperature for 60 minutes using a volume of 0.125N sodium hydroxide, providing 5% NaOH on an ovendry wood basis. The products were collected on sintered-glass funnels, washed, left to stand in water 2 hours, filtered, covered with 3% aqueous acetic acid for about 2 hours, filtered, and washed. Yield data are included in Table I.

Separation into individual fibers was achieved after alkali extraction without difficulty in a British disintegrator as part of the procedure used and outlined in Table II before preparing handsheets. Beating in the Valley beater was carried out in accordance with TAPPI Standard Method T 200 ts-66.

Handsheet Preparation and Testing

After the pulps were beaten to obtain data as in Table II, handsheets were prepared according to TAPPI Standard Method T 205 m-58.

Handsheet test data given in Table III were obtained according to TAPPI Standard Method T 220 m-60. Opacities were determined according to TAPPI Standard Method T 425 m-60 (Opacity of Paper) where:

$$\text{contrast ratio } C_{0.89} = 100 \frac{R_B}{R_W} ,$$

using a Bausch & Lomb Opacimeter. Zero-span tests were carried out according to TAPPI Standard Method T 481 sm-60 using handsheets with a nominal basis weight of 50 g./m.^{2} (o.d.).

Reacted Chips and Microscopic Examination

The chip used in preparing the specimen shown in Fig. 2 was one of those extracted with solvent, then reacted with chlorite, as detailed under Pulp 1 in Report Three, page 28, Table VIII. After Stage II, the washed chip was freeze dried, embedded directly in butyl methacrylate, and mounted in mineral oil.

OBSERVATIONS ON FIBERIZED ASPEN

DISCUSSION

Some Questions with an Approach to Answers

In Report One, page 11, there was considered a series of experiments involving the reaction of aspen with chlorite which showed that at the 3% Klason lignin level prior extraction with 0.125-0.5N sodium hydroxide resulted in an apparent three- to fourfold increase in carbohydrate removal compared with prior extraction with water. Then, later on, by using analytical data to obtain a material balance on solvent-extracted aspen meal reacted for different times at 65°C. with sodium chlorite, it was deduced, as recorded in Report Three, from the difference between yield and carbohydrates that there was a significant amount of material missing. This could be accounted for through a modified lignin analysis based on the work described by Buchanan in Report Two.

Thus, one question that arose concerns the extent to which the apparent three- to fourfold increase in removal of carbohydrates by prior extraction with alkali is discounted either when modified lignin analyses are taken into account or for some other reason.

In Report One, page 17, data were also presented showing the effect of caustic extraction on the rate of delignification with chlorite, using aspen shreds. Thus, another question concerns how such rates are influenced by the use of fiberized chips.

In Report One, page 23, it was also shown when pulping aspen shreds that the difference between total yield and screened yield varied from 1 to 24% for a total yield range of 69-75%. This raises a question of whether there is some critical phenomenon associated with these data. Later it was demonstrated through stepwise delignification combined with high-consistency defibering and without initial caustic extraction that screen rejects could be reduced to an acceptable amount at the 80%-yield level, as recorded in Report Three. At the same time, it was found that handsheet strength data were improved by further extraction with caustic solution which was accompanied by a lowering of yield and significant changes in fiber morphology.

This previous work did not provide adequate answers to the questions already raised. To obtain a better appreciation of the interplay of alkali and reaction of lignin with chlorine dioxide with respect to modified lignin content, yield, and screen rejects, an experiment was planned to give a general picture of the area. The data obtained are presented in Table IV, from which it is seen that the maximum amount of alkali used in the extraction prior to reaction with chlorite was 6%. For the conditions used, this corresponded to 0.09N sodium hydroxide solution, which would be expected to result in at least an apparent twofold increase in carbohydrate removal compared with prior extraction with water on the basis of the data in Report One, page 13. The times of reaction with chlorite were chosen with the intention of straddling a yield range hopefully achievable using a more favorable amount of chlorine dioxide. Alkali extraction conditions after reaction with chlorite were selected on a semiarbitrary basis using the information already available.

Influence of Alkali Pretreatment on Carbohydrate Removal

The data in Table IV confirmed that after reaction with chlorite, at a Klason lignin level of, say, 2.5%, prior extraction with 0.09N sodium hydroxide resulted in an apparent increase in carbohydrate removal compared with prior extraction with water. However, modified lignin analyses revealed that a notable

TABLE IV

OXIDATIVE DELIGNIFICATION OF FIBERIZED ASPEN WITH CHLORITE

Stage I (Pretreatment)

Consistency, 6.0%[a] Time, 1 hr. at ambient temp.

Pulp	A	B	C
Sodium hydroxide, %	nil (water)	3.0	6.0
pH at 5 min.	7.3	12.2	12.7
pH at 60 min.	7.3	9.5	9.4

Stage II (Chlorite)

Consistency, 6.0%; chlorite, 100 w/w %; temp., 50°C.; initial pH, 4.5 (acetic acid)

Pulp	A1	A2	A3	A4	A5	B1	B2	B3	B4	B5	C1	C2	C3	C4	C5
Time, hr.	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Final pH	4.9	5.2	5.3	5.2	5.4	4.9	5.1	5.3	5.2	5.5	5.0	5.2	5.3	5.3	5.5
Yield, %	94.0	90.0	88.0	87.0	86.5	89.5	86.0	84.5	82.5	82.0	86.5	82.0	80.5	80.0	80.0
Klason lignin, %	7.3	--	3.3	--	2.3	6.4	--	2.7	--	1.9	5.9	--	2.5	--	1.8
Mod. lignin (Buchanan)[b]															
Acetone-sol.	14.8	--	13.1	--	11.9	15.6	--	11.8	--	10.2	11.4	--	7.1	--	7.0
Klason	2.6	--	1.0	--	0.9	2.8	--	1.9	--	1.4	1.1	--	--	--	1.3
Acid-sol.	1.7	--	1.2	--	1.1	1.5	--	1.3	--	1.1	1.5	--	--	--	1.0
Total	19.2	--	15.4	--	13.9	19.9	--	15.0	--	12.8	14.0	--	--	--	9.4
Graff's "C" stain		yellow → olive green					lt. purple → med. purple					purple → dark purple			

Stage III (Posttreatment)

Consistency, 8.0%; time, 1 hr. at 50°C.

Pulp	A1	A2	A3	A4	A5	B1	B2	B3	B4	B5	C1	C2	C3	C4	C5
Sodium hydroxide, %[c]	9.0	--	9.0	--	9.0	6.0	--	6.0	--	6.0	3.0	--	3.0	--	3.0
Sodium hydroxide, %[d]	--	6.0	--	6.0	--	--	3.0	--	3.0	--	--	0	--	0	--
Final pH[c,e]	12.2	11.1	12.3	11.1	12.5	12.3	11.0	12.5	11.3	12.4	12.3	5.4	12.4	5.5	12.4
Yield, %[c,e]	72.0	--	67.0	--	66.5	71.0	--	67.5	--	66.0	74.0	--	67.5	--	68.0
Yield, %[d,e]	--	72.0	--	70.0	--	--	74.0	--	69.0	--	--	79.0	--	77.5	--
Brightness, GE	--	73.2	--	76.3	--	--	72.3	--	77.0	--	--	75.8	--	81.2	--
Canadian freeness	--	550	--	470	--	--	560	--	450	--	--	750	--	600	--
Fiber separation	??	?	+	+	+	??	?	+	+	+	??	?	+	?	+
Klason lignin, %	1.7	--	0.4	--	0.2	1.6	--	0.3	--	0.2	2.1	--	0.3	--	0.2
Modified lignin (Buchanan)[b]															
Acetone-sol.	1.2	--	1.0	--	0.9	2.0	--	1.5	--	0.9	2.0	--	0.7	--	0.6
Klason	1.6	--	0.5	--	0.5	1.6	--	1.3	--	0.9	2.7	--	0.9	--	1.2
Acid-sol.	1.3	--	0.8	--	0.8	1.6	--	0.9	--	0.9	1.8	--	0.8	--	0.8
Total	4.1	--	2.3	--	2.2	5.2	--	3.7	--	2.7	6.4	--	2.4	--	2.6

[a] All percentages on fiberized chip basis. [b] Mean of two determinations. [c] Total sodium hydroxide applied in Stages I and III, 9.0%.

[d] Total sodium hydroxide applied in Stages I and III, 6.0%. [e] All pulps stained blue with Graff's "C" stain.

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amount of noncarbohydrate material was unaccounted for by the Klason lignin analyses. A significant portion of the modified lignin remaining after reaction with chlorite was shown by the data obtained on the extracted pulps to be removed by alkali and the data in Table IV gave no indication of final yields or carbohydrate content being higher when prior extraction with alkali was omitted.

Influence of Alkali Pretreatment on Rate of Reduction in Residual Klason Lignin

In considering the effect of caustic pretreatment on Klason lignin content, the data can be represented as in Fig. 4. Because the previous observation that alkali extraction substantially increased the rate of reduction in the residual Klason lignin of shreds (Report One, page 17), it is surprising at first to find the slopes of the curves in Fig. 4 are similar, although displaced downward on the ordinate by caustic extraction. The explanation is believed to reflect the fact that with fiberized chips, the extent to which the Klason lignin content is reduced by excess chlorite is no longer dominated by the dimensions of the wood material. This implies that in a reaction with chlorite for an equal time, shreds would be expected to contain more Klason lignin than fiberized chips, as is the case. For example, Report One, Fig. 6, shows shreds contained about 10% Klason lignin, whereas fiberized chips would contain 2.6% (Fig. 4) after reaction at 50°C. for four hours.

Liberation of Fibers

When the relationships between yield, carbohydrates, and total modified lignin data are represented as in Fig. 5, an interesting situation is disclosed. The three products, A3/III, B1/III, and C1/III, which were obtained by reaction for one hour with chlorite followed by alkaline extraction, fall within a circle with yield above 70% and were similar in that they showed little indication of being easily separated into individual fibers. In contrast, the related products A3/III,

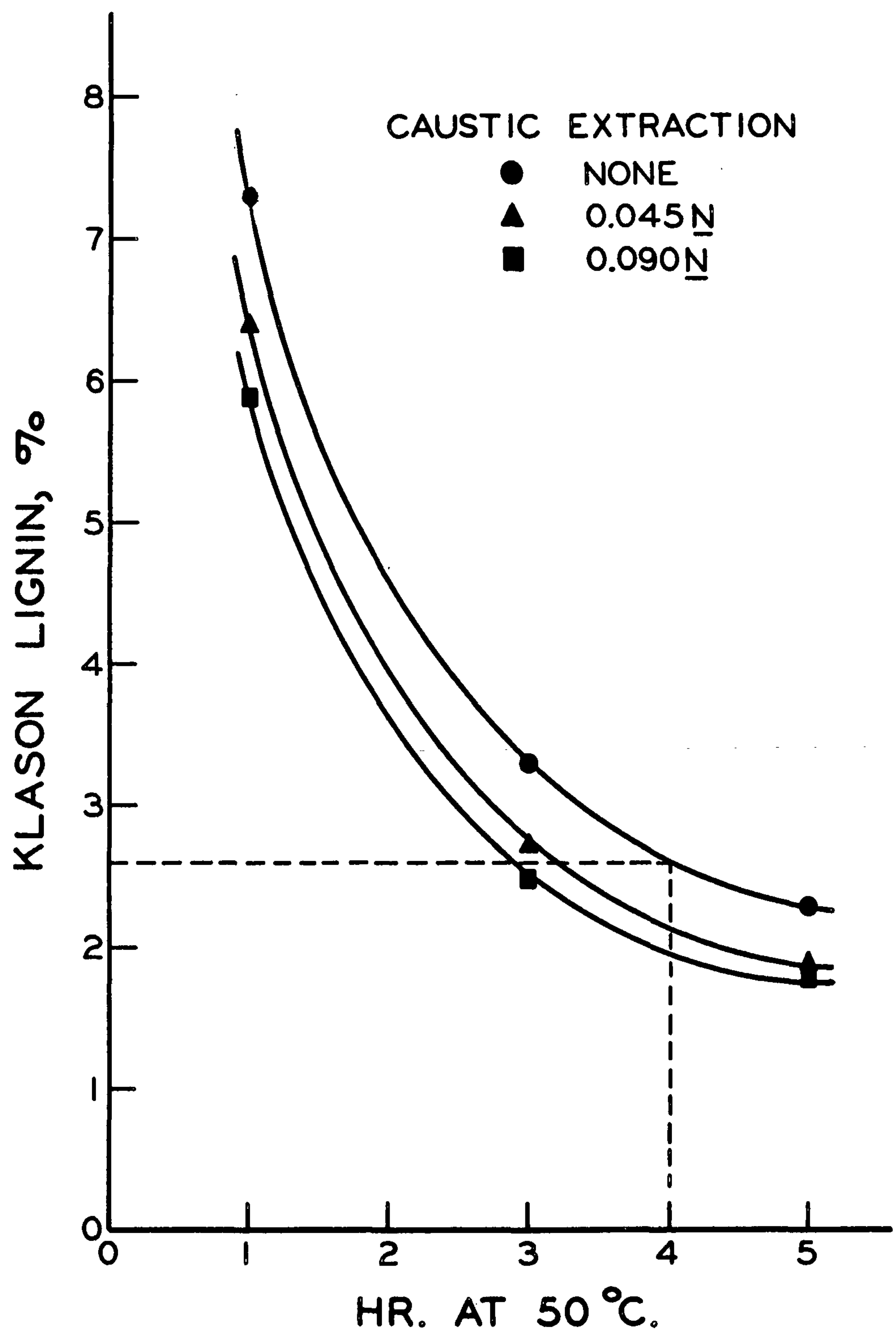

Figure 4. Effect of Caustic Extraction on Klason Lignin Content After Reaction with Chlorite

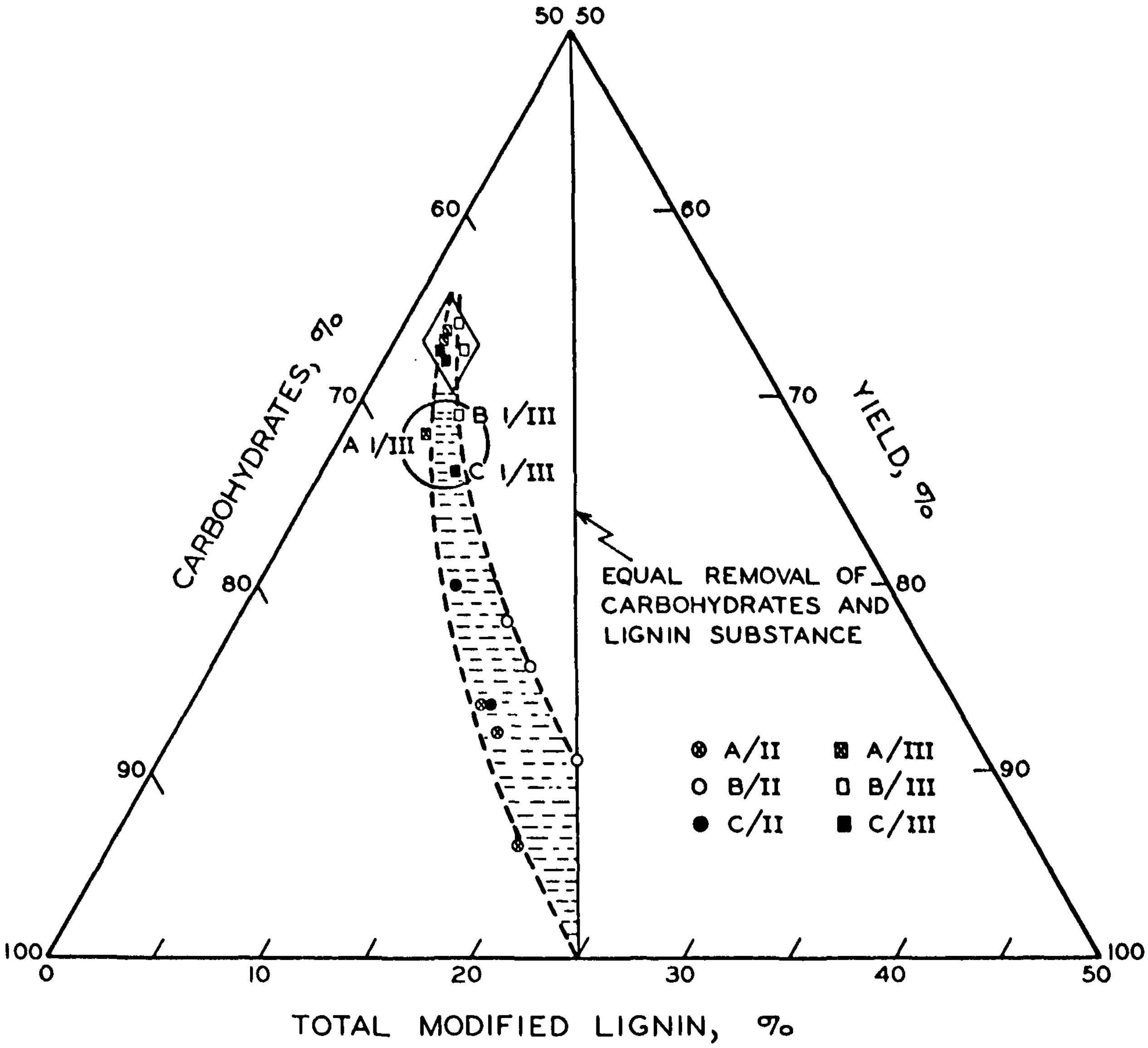

Figure 5. Relative Removal of Modified Lignin by Chlorite Oxidation and Alkaline Extraction. Pulps Within Diamond Separated into Individual Fibers, Whereas Pulps Within Circle Contained Many Shives

A5/III, B3/III, B5/III, C3/III, and C5/III are all represented in Fig. 5 within a diamond-shaped area falling between about 65 and 70% yield, and all these products were similar in being apparently separable into individual fibers through visual examination after disintegration. Thus, it seems that somewhere near 65-70% yield individual fibers are liberated without significant mechanical force by the combined reaction of chlorite and alkali. Looked at another way, it might be stated that for a total yield range of 69-75%, screen rejects could conceivably vary to a considerable degree, as was noted above regarding some data in Report One. All of the modified lignin and corresponding yield data in Table IV were found to fall within an area representing the removal of more lignin than carbohydrate. In addition, this area converged to a point so that differences in the amount of carbohydrates at constant modified lignin content progressively diminished as the total modified lignin decreased.

Delignification with Aqueous Chlorine Dioxide and Alkali

After reviewing both the data covering earlier experiments on stepwise delignification presented in Report Three, Tables XI, XVI, and XIX, and the above observations on fiberized aspen, it was decided to subject this material to reaction with 9% aqueous chlorine dioxide (o.d. f.c. basis) in a single step. In addition, on either side of this step, there would be alkaline extractions along the lines used in Table IV. The data obtained from two series of experiments, namely, GG-1|GG-2|GG-3 and II-1|II-2|II-3, are presented in Table V. From the first experiments it could be seen that the yield data after reaction with 9% chlorine dioxide approximated those in Table IV corresponding to reaction with chlorite for about one hour. This implied that following alkaline extraction, the product may be difficult to separate into fibers, which was found to be so, except where 6.0% sodium hydroxide was used before and after oxidation. The second series of

TABLE V

DELIGNIFICATION OF FIBERIZED ASPEN WITH AQUEOUS CHLORINE DIOXIDE AND ALKALI

Stage I (Pretreatment)

Consistency, 6.0 w/w %   Time, 60 min.

Pulp	Fiberized Aspen	GG-1	GG-2	GG-3	II-1	II-2	II-3
Sodium hydroxide, %		0	3.0	6.0	0	3.0	6.0
Temp., °C.		25	25	25	50	50	50
pH after 5 min.		5.7	12.2	12.7	5.8	11.7	12.0
Final pH		5.3	11.7	12.5	5.4	10.5	11.8
Yield, %[a]		98.2	93.0	90.7	99.4	95.5	90.2
Klason lignin, %		--	--	--	22.2	21.0	19.9
Modified lignin analysis							
Acetone-sol., %	5.2	--	--	--	4.8	3.0	3.2
Klason, %	17.9	--	--	--	19.3	18.3	17.7
Acid-sol., %	1.9	--	--	--	1.5	1.5	1.3
Total, %	25.0	--	--	--	25.6	22.8	22.2

Stage II (Chlorine dioxide)

Consistency, 5.0%   Chlorine dioxide, 9%
Initial temp., 25°C.   Temp. after 60 min., 35°C.

	GG-1	GG-2	GG-3	II-1	II-2	II-3
Sodium hydroxide, %	5.0	3.0	3.0	5.0	3.0	3.0
pH after 5 min.	6.5	6.4	6.5	7.2	6.6	7.1
Final pH	4.0	3.3	3.2	4.0	3.1	3.2
Time, min. (starch-iodide)	290	260	260	300	295	290
Yield, %	92.2	87.3(?)	87.1	94.3	91.0	85.4
Klason lignin, %	--	--	--	13.8	11.8	10.6
Modified lignin analysis						
Acetone-sol., %	--	--	--	14.8	17.5	14.8
Klason, %	--	--	--	6.5	4.4	4.1
Acid-sol., %	--	--	--	1.5	1.4	1.2
Total, %	--	--	--	22.8	23.3	20.1

Stage III (Alkaline extraction)

Consistency, 8.0 w/w %   Time, 60 min.
Temp., 50°C.

	GG-1	GG-2	GG-3	II-1	II-2	II-3
Sodium hydroxide, %	6.0	3.0	6.0	9.0	6.0	3.0
pH after 5 min.	11.9	10.6	11.9	12.6	12.2	11.5
Final pH	10.3	8.9	11.5	12.1	11.6	10.6
Yield, %	73.9	78.6	65.5	72.8	69.0	73.7
Screen rejects, % o.d. pulp	35.6[b]	39.5[b]	6.1[b]	12.5[c]	3.6[c]	12.0[c]
Klason lignin, %	--	--	--	5.3	3.3	4.8
Modified lignin analysis						
Acetone-sol., %	--	--	--	2.6	2.2	3.4
Klason, %	--	--	--	4.7	2.9	3.5
Acid-sol., %	--	--	--	1.1	1.0	1.1
Total, %	--	--	--	8.4	6.1	8.0

Stage IV (Alkaline extraction)

Consistency, 8.0 w/w %   Time, 60 min.
Temp., 50°C.

	GG-1	GG-2	GG-3	II-1	II-2	II-3
Sodium hydroxide, %	3.0	3.0	--	3.0	--	3.0
pH after 5 min.	12.0	11.9	--	--	--	--
Final pH	11.7	11.4	--	11.9	--	11.8
Yield, %	65.8	69.4	--	69.7	--	65.9
Screen rejects, % o.d. pulp	22.9[b]	19.9[b]	--	9.4[c]	--	6.2[c]

[a] All percentages on an o.d. fiberized chip basis.

[b] After 500 counts in British disintegrator. [c] After 1000 counts.

experiments had a higher temperature for the alkaline extraction before oxidation and 9% of sodium hydroxide was split 0-9, 3-6, and 6-3 before and after oxidation. It appeared from the data that the most favorable fiber separation was obtained with a 3-6 split.

The relationships between lignin and yield for II-1, II-2, and II-3 (Table V) are shown in Fig. 6, in which the difference between lignin content and yield is represented as carbohydrates. Lignin is expressed both as Klason lignin and as total modified lignin, the data obtained from the same product being bridged by tie-lines. It can be seen from Fig. 6 that a large part of the difference between the two methods of expressing lignin content no longer exists after alkali extraction following reaction with chlorine dioxide. This reflects the removal of modified lignin by alkali. It is also evident that lignin which is degraded, yet still detectable as usual in a Klason lignin analysis, is sufficiently degraded to be alkali soluble.

In keeping with the observations made concerning Fig. 5, it again appears from the data in Table V that an easily defiberable product can be obtained somewhere in the 65-70% yield range.

Handsheet Data on a Holopulp

To gain an insight into what kind of pulp might be obtained in three chemical stages using 9% chlorine and alkali extraction without resorting to mechanical defibration at a high consistency, sufficient pulp was prepared to provide the data presented in Table VI. For comparison, a kraft pulp was made from the same lot of aspen chips and handsheet data were obtained as in Table VII.

The handsheet test data obtained from small aspen chips (Table III) plus those from Tables VI and VII are compared graphically in Fig. 7, 8, and 9. In

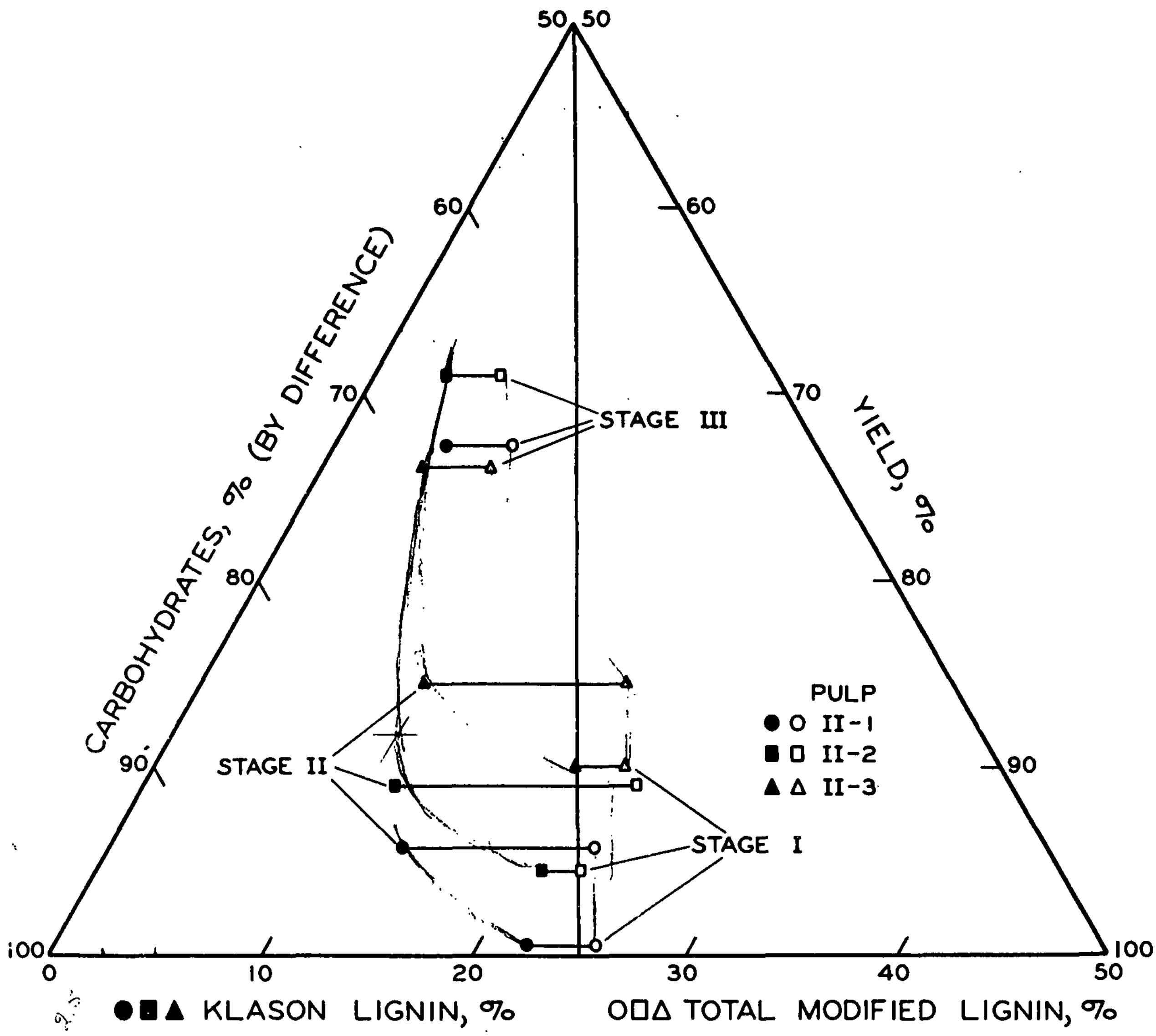

Figure 6. Relative Removal of Klason and Modified Lignin by Chlorine Dioxide Oxidation and Alkali Extraction. The 69% Yield Pulp Disintegrated into Fibers Most Readily

TABLE VI

DELIGNIFICATION WITH CHLORINE DIOXIDE/ALKALI AND PULP EVALUATION

Pulp preparation: As for Pulp II-2 (Table V)

Yield, %:	Stage I	95.2
	Stage II	90.3
	Stage III	70.6 with 7.5% screen rejects after disintegration in British disintegrator for 600 counts
GE brightness		49.6

Handsheet Data (EDE Pulp)

Canadian freeness/min.[a]	590/0	490/6	370/16	305/22	205/32
Density, g./cc.	0.593	0.648	0.702	0.734	0.766
Opacity, %	77	77	76	74	69
Breaking length, m.	4700	6800	8500	8900	10,000
Burst factor, TAPPI	17	31	42	46	54
Tear, TAPPI	62	59	56	55	50
Zero-span breaking length, km.	12.7	14.7	17.4	17.7	16.9

[a] 2-Kg. weight on Valley beater.

TABLE VII

PREPARATION OF ASPEN KRAFT PULP FOR REFERENCE

Liquor/wood	4.0	Max. temp., °C.	174
Active alkali, % Na_2O	19.4	Time to 174°, min.	90
Sulfidity, %	30.0	Time at 174°, min.	120
Blowdown to 80 p.s.i., min.	5	Unscreened yield, %	50.5
Kappa no.	11.2	Rejects, %	0.2

Handsheet Data

Canadian freeness/min.	600/0	530/5	470/10	340/20	185/35
Density, g./cc.	0.596	0.655	0.690	0.765	0.852
Breaking length, km.	5.55	7.23	8.33	9.99	10.60
Burst factor, TAPPI	21	31	41	57	65
Tear factor, TAPPI	58	70	74	73	59
Zero-span breaking length, km.[a]	20.0	20.9	20.6	20.0	19.7

[a] In a study of 66 Populus tremuloides trees 31 years or more in age, zero-span breaking length for kraft pulps was found to average 18.4 km. and have a 15.0 to 23.3-km. range (4).

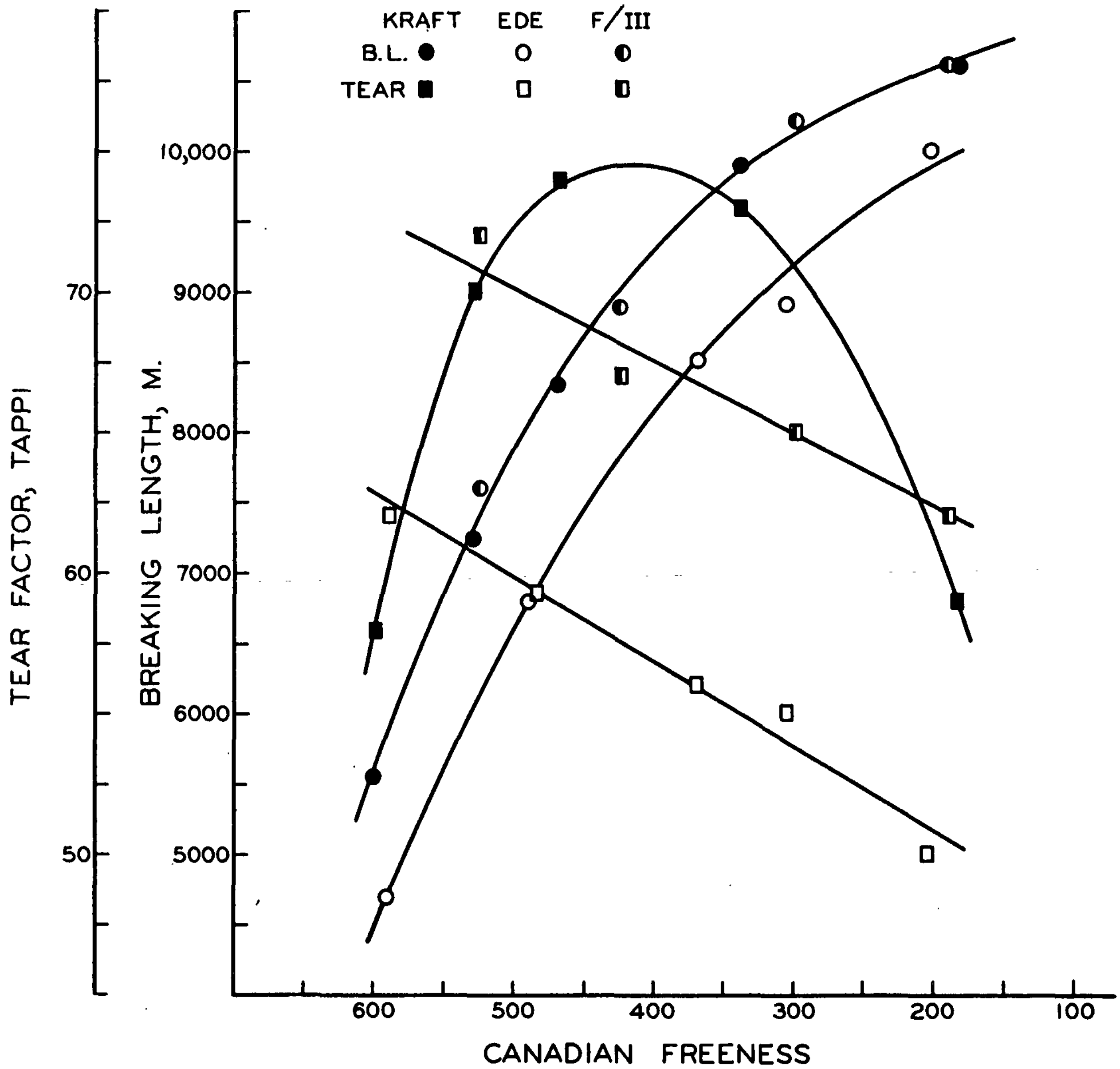

Figure 7. Relationships Between Tear, Breaking Length, and Freeness for 50% Yield Aspen Kraft Pulp, 70% Yield Chlorine Dioxide Pulp (EDE), and 64% Yield Chlorite Pulp (F/III)

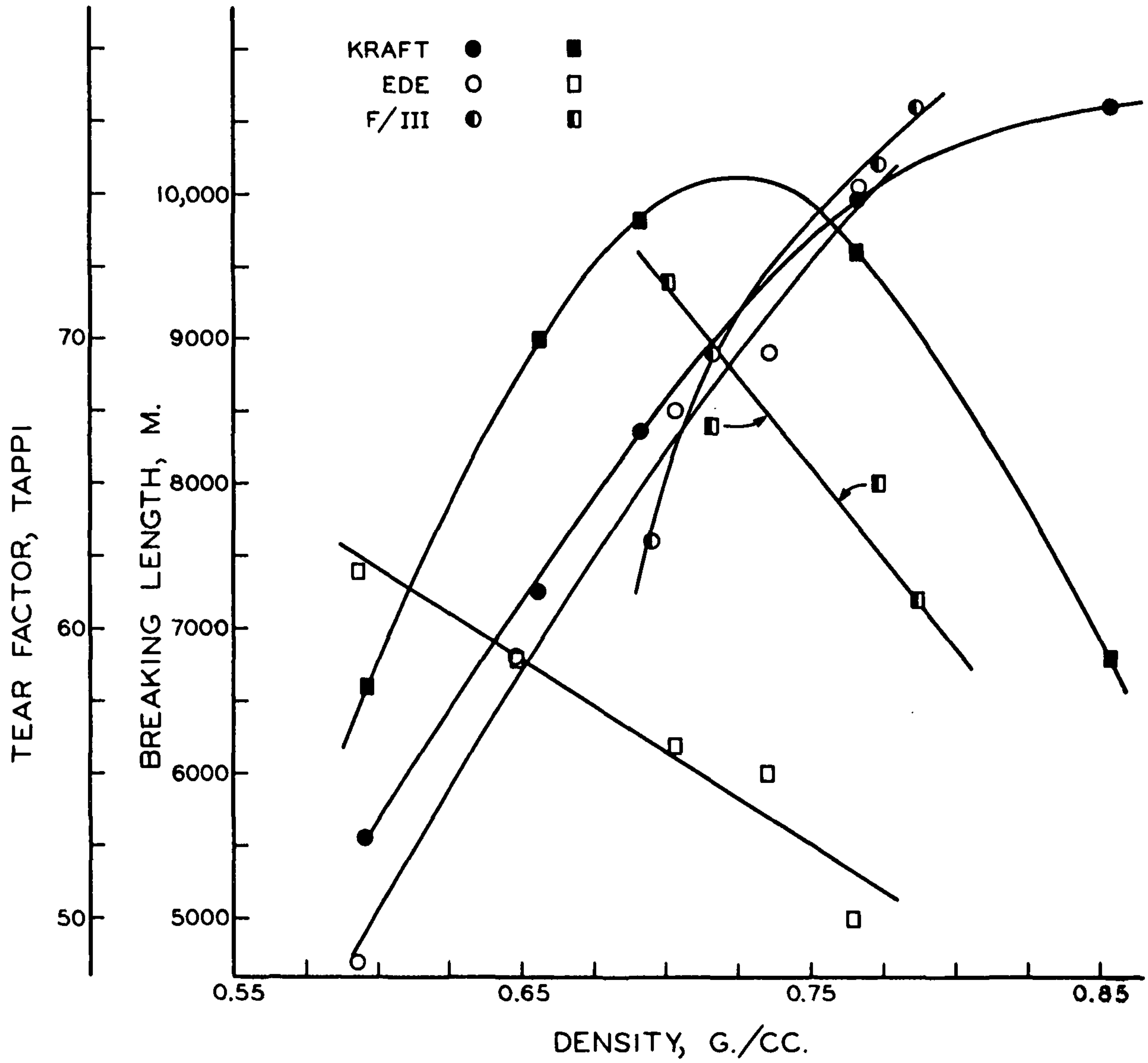

Figure 8. Relationships Between Tear, Breaking Length, and Sheet Density for 50% Yield Aspen Kraft Pulp, 70% Yield Chlorine Dioxide Pulp (EDE), and 64% Yield Chlorite Pulp (F/III)

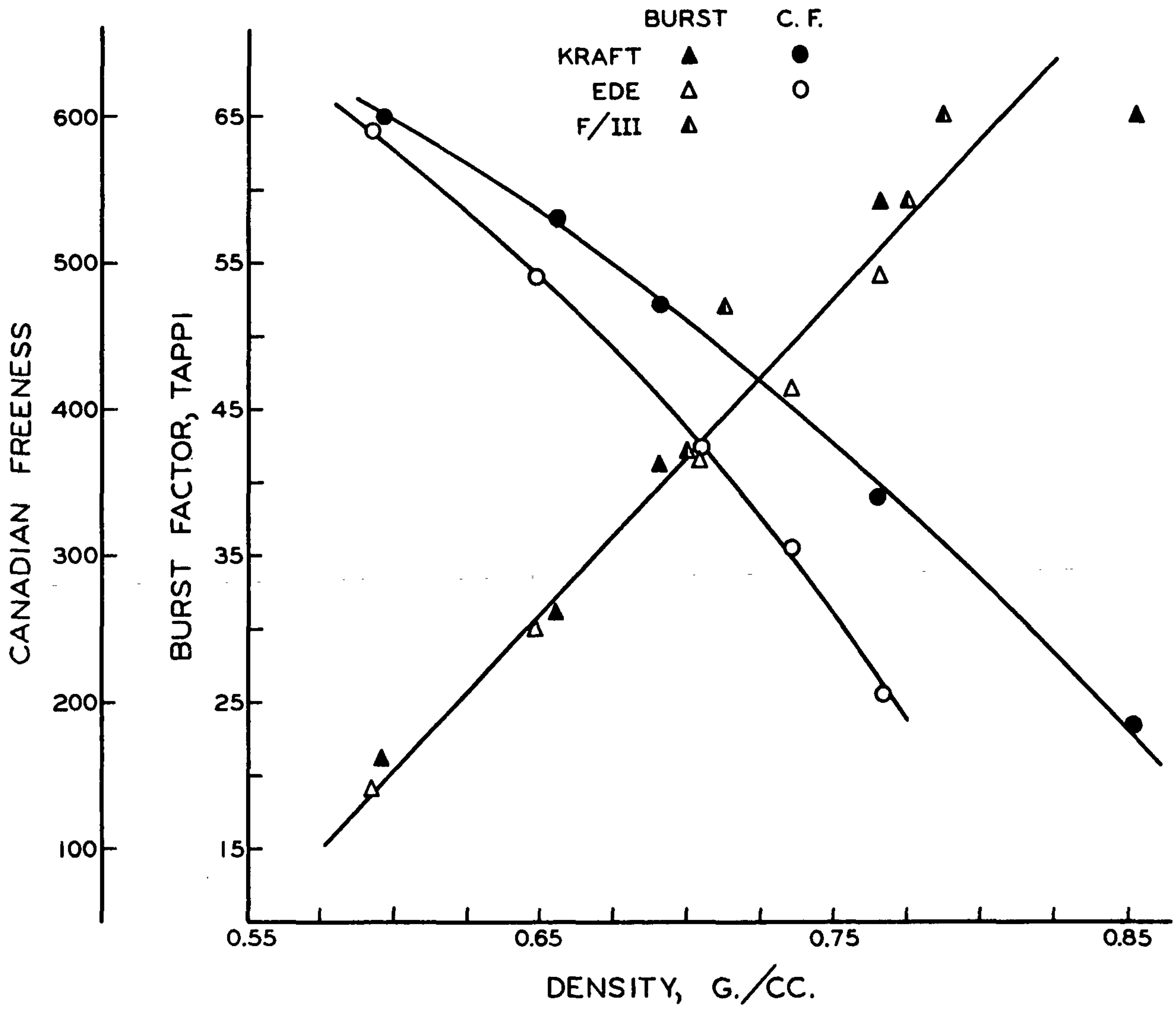

Figure 9. Relationships Between Burst, Freeness, and Sheet Density for 50% Yield Aspen Kraft Pulp, 70% Yield Chlorine Dioxide Pulp (EDE), and 64% Yield Chlorite Pulp (F/III)

Fig. 7 and 8, the relationships of tear factor and breaking length are compared with freeness (Fig. 7) and sheet density (Fig. 8). The tear factor curve for the aspen kraft pulp has the familiar paraboloid shape, whereas the curves for the other two pulps have a slope similar to that for the kraft pulp after it passes the maximum. It is of note that the tear curve for the chlorite pulp (F/III) intercepts the corresponding curve for kraft pulp near its maximum, which indicates that better results should be achievable for a chlorine dioxide-alkali pulp than those shown. Breaking lengths for the three pulps overlapped between 8500 and 10,000 meters. As seen from Fig. 9, the three pulps had a similar linear relationship between burst factor and sheet density. However, as burst increased, the freeness of the kraft pulp was reduced less for twice the bedplate load used on the other pulp.

It appears appropriate to note that if a 70% total yield pulp with a zero-span breaking length of 17 km., as in Table VI, is compared with a 50%-yield kraft pulp with a zero-span breaking length of 21 km., as in Table VII, the latter would have a value of 15 km. on an equal fiber count basis. The values recorded in Table III are approximately 30% greater, indicating that more of the individual fiber strength has been retained in the chlorite-alkali pulps made from fiberized chips.

Alkali Pretreatment and Chlorine Dioxide Consumption

Although the conditions used to prepare pulp for the handsheets made to obtain the data in Table VI were selected on the basis of the most favorable indications from the information available at the time, it is not particularly clear from the results in Tables IV and V that pretreatment with alkali is necessary. It appears from Fig. 4 that caustic extraction followed by reaction with the same amount of chlorine dioxide does lead to the retention of less Klason lignin. This implies the alkali extractives of aspen would consume chlorine dioxide in an uncertain amount. Experiments showed that alkali extractives were capable of consuming up to 0.66% chlorine dioxide on a fiberized chip basis, as recorded in Table VIII.

TABLE VIII

CONSUMPTION OF CHLORINE DIOXIDE BY ASPEN ALKALI EXTRACTIVES

Time, min. at 50°C.	10	40	60
Chlorine dioxide, g./100 g. o.d. fiberized chips	0.15	0.58	0.66

While this amount of chlorine dioxide consumption is too large to be ignored, by-passing the pretreatment with alkali is also under study, one experiment using gaseous chlorine dioxide having been described in Report Five.

EXPERIMENTAL

Raw Materials

Chip Lot A3/55 was used to prepare unscreened fiberized aspen chips according to the procedure in Report Three, page 55.

Delignification with Chlorite and Alkali

The on-6-mesh portion of fiberized chips (100-g. o.d. lots) was extracted with water or alkali using the conditions given in Table IV, collected on a funnel, then washed with tap water and centrifuged. Each lot was subdivided, reacted with chlorite solution as prepared previously; then after the time shown in Table IV the product was collected in a Buchner funnel, washed with 6 x 0.5 liters of distilled water and air dried. Subsequently, the fifteen products obtained were treated as shown in Table IV, and washed with distilled water. The tendency for fiber bundles to separate into individual fibers was judged subjectively as positive, questionable, or very questionable. Samples on which Canadian freeness values were to be determined were stirred at moderate speed in a Waring Blendor at 3% s.c. for 1 min., soaked in distilled water overnight, beaten for 600 rev. counts in a British disintegrator, screened on a 0.006-in. screen, and the accepts collected on a sintered-glass funnel.

Delignification with Aqueous Chlorine Dioxide and Alkali

Unscreened fiberized aspen chips were delignified using the conditions set out in Table V. Between stages, the fibrous product was collected on a funnel, then washed with deionized water at the temperature used in the preceding stage, and after that with cold water. In addition, the washed products obtained after alkali extraction of modified lignin were covered with 3% acetic acid for 30 min., filtered, and washed with deionized water. Disintegrated products were screened on a 0.006-in. flat screen.

Data from a Holopulp and Handsheets

Unscreened, fiberized aspen chips, as above, were used to prepare a holopulp as in Table VI. Handsheet preparation and testing were carried out according to the methods defined in the previous experimental part.

Aspen Kraft Reference Pulp

Using chips from Lot A3/55, a kraft pulp was prepared in a vertical batch, stainless steel digester of about 2-cu. ft. capacity, fitted with a pump and heat exchanger for external heating of the liquor. Other details are included in Table VII.

<u>Reaction of Aspen Alkali Extractives with Chlorine Dioxide</u>

Alkali filtrate, obtained from aspen extracted with 3% sodium hydroxide as for Pulp II-2 in Table V, was concentrated under reduced pressure in a rotary evaporator and then freeze dried.

Found:

0.57% total solids

0.08% sodium hydroxide (calculated from sulfate ash)

0.49% organic solids (by difference).

The freeze-dried soluble solids were insoluble in acetone, ether, benzene, and ethanol, partially soluble in glacial acetic acid, and readily soluble in water.

Consumption of chlorine dioxide (concentration = approx. 1 g./liter) by the freeze-dried solids was calculated from the difference in the titratable amount of chlorine dioxide present in a blank and in a solution containing a known amount of organic solids. This reaction was carried out at 50°C. and pH 4. In calculating the chlorine dioxide consumption, an organic content of freeze-dried solids equivalent to 5% of o.d. fiberized chips was assumed. The results are given in Table VIII.

CAUSTIC EXTRACTION AFTER CHLORINE DIOXIDE REACTION (5)

DISCUSSION

Preliminary Study

In the previous part it was established that if alkali-extracted fiberized aspen chips are reacted in water with 9.0% chlorine dioxide, the lignin can be modified sufficiently to make an appreciable part soluble in alkali at 50°C. and for a 65-70% yield individual fibers appear to be liberated. While both opacity and freeness of this kind of pulp were satisfactory, the brightness was low. Thus, one question concerns what can be achieved by bleaching. Before considering this, it is logical to know more about how alkali extraction conditions influence yield, unbleached fiber properties, fiber liberation, removal of modified lignin, and retention of carbohydrates. Since bleaching will be concerned with lignin removal, extraction of modified lignin probably should be as complete as possible, while carbohydrate retention probably should be as great as possible.

As part of a study on the role of caustic extraction, fiberized aspen chips, which had been extracted with alkali then reacted in water with 9.0% chlorine dioxide, were extracted at 50 and 60°C. for various times, and information obtained as presented in Table IX.

From the final pH data it is apparent an adequate amount of alkali was present at the end of each experiment to permit conversion of acidic degradation products to the more soluble sodium salt. Therefore, it is evident from Table IX that time and temperature of caustic extraction both influence total yield and screen rejects.

TABLE IX

ROLE OF CAUSTIC EXTRACTION: TIME, TEMPERATURE, YIELD, AND REJECTS

I. Alkali Extraction of Fiberized Chips (LL-0)

As for Pulp II-2 in Table V; yield, % (LL-1) - 96.4[a]

II. Chlorine Dioxide Reaction (on LL-1)

Chlorine dioxide, %	9.0	Sodium hydroxide, %	3.5
Initial temp., °C.	25	Consistency, %	5.0
Temp. after 0.75 hr.	35	pH after 5 min.	6.5
Time, hr.	4.5	Final pH	3.0
Yield, % (LL-2)	90.7		

→ Klason lig. 13.0, acid [illegible], 5.0 — total 18.0
Mod. lig.: Acetone [illegible], 9.1; K.L. [illegible]; [illegible] 2.0 — total 17.1

III. Alkali Extraction (LL-2)

Sodium hydroxide, 5.8%; consistency, 8.3%.

Time, hr.	Final pH 50°C.	Final pH 60°C.	Yield, % 50°C.	Yield, % 60°C.	Rejects, %[b] 50°C.	Rejects, %[b] 60°C.
0.1	11.8	11.7	79.3	75.6 (72.6)[c]	13.7	9.6
0.2	11.8	--	77.2	75.6 (72.7)[c]	11.7	7.8
0.3	--	11.5	--	73.6	--	6.6
0.5	11.7	11.6	74.9	72.6	7.2	6.1
1.0	11.7	11.5	72.9	72.1	5.8	4.5
2.0	11.7	11.4	72.6	72.6	4.1	4.5
4.0	11.1	10.7	72.7	73.0 (67.8)[c]	3.7	3.9

[a] All percentage data on o.d. fiberized chip basis unless noted to contrary.

[b] Data on o.d. product, Stage III basis.

[c] Original data obtained after washing with cold water, then adding 100 ml. of 5% aqueous acetic acid per 40 g. o.d. fiberized chips. Yield values shown in parenthesis obtained by substituting a hot (50-60°C., pH 9-9.5) for the cold water wash. The hot water washed pulps drained [illegible] the 40 [illegible] (67.8% yield) was [illegible] [illegible] [illegible]

Influence of Extraction Time on Handsheet Data

To clarify further how extraction time may influence the handsheet properties of a pulp, results as in Table X were obtained. From these it can be seen that a more bulky sheet with lower breaking length is made when a higher yield pulp is produced. This is reminiscent of what occurs when, for example, less readily defibered kraft pulps of higher yield are made. Examination of the handsheets prepared from Pulps LL-10, LL-60, and LL-240 revealed a noticeable decrease in the number of fiber bundles with beating. The increase in zero-span breaking length with more beating is consistent with this observation. Thus, the time of caustic extraction at 50°C. after modification of lignin by chlorine dioxide influences unbleached pulp properties as well as yield and screen rejects.

It is noted that the data in Table X for Pulp LL-60 ideally should be the same as the handsheet data in Table VI, whereas comparison reveals some differences. These are not large and may arise from more than one source including differences between chip fiberization on one occasion compared with another. Using the same lot of chips, identified as "A3/55," three of the batches of fiberized chips made in connection with this report are identified in Table XI. When chips were fed to the Bauer at a more even, slower rate, there was a reduction in the amount of the coarsest fraction without a significant increase in the finest material. This is the only change introduced recently in the technique for making fiberized chips, since at present attention is being focused in other areas of this project.

TABLE X

ROLE OF CAUSTIC EXTRACTION: HANDSHEET DATA

I. Alkali Extraction of Fiberized Chips (LL-0)

Yield 96.4% (LL-1), as in Table IX

II. Chlorine Dioxide Reaction on LL-1

Yield 90.7% (LL-2), as in Table IX

III. Alkaline Extraction of LL-2

Sodium hydroxide = 6.0%; consistency = 8.0%; temp. = 50°C.

Time, min.	10 (LL-10)	60 (LL-60)	240 (LL-240)
Final pH	11.8	11.7	11.6
Yield, %	73.0	69.0	67.6
Rejects, % o.d. pulp	7.0	2.8	2.2

Handsheet Data

Canadian freeness/min.[a]	LL-10	560/0	460/6	350/20	210/38
	LL-60	565/0	465/6	345/20	205/38
	LL-240	515/0	440/6	325/20	205/35
Density, g./cc.	LL-10	0.585	0.633	0.691	0.749
	LL-60	0.625	0.673	0.721	0.790
	LL-240	0.628	0.691	0.747	0.756
Opacity, %	LL-10	82	83	81	78
	LL-60	81	80	78	72
	LL-240	80	80	78	76
Breaking length, km.	LL-10	4.80	6.30	8.20	9.00
	LL-60	5.30	7.00	8.70	9.20
	LL-240	5.90	7.40	9.10	9.20
Burst factor, TAPPI	LL-10	21	29	40	48
	LL-60	23	34	45	53
	LL-240	27	36	49	53
Tear, TAPPI	LL-10	62	61	57	51
	LL-60	65	62	56	51
	LL-240	64	59	56	54
Zero-span breaking length, km. [approx. 50 g./m.^{2} (o.d.)]	LL-10	12.4	15.4	16.0	17.6
	LL-60	13.2	15.7	16.9	18.1
	LL-240	14.6	16.1	17.5	17.7

[a] Two-kg. weight on Valley beater.

TABLE XI

BAUER-McNETT CLASSIFICATIONS OF FIBERIZED ASPEN CHIPS

Screen	% a	% b	% c
On 6 mesh	29.9	24.5	11.8
On 12 mesh	17.9	21.3	22.4
On 35 mesh	24.2	26.1	35.8
On 65 mesh	9.8	9.2	9.4
Through 65 mesh (by diff.)	18.2	18.9	20.6

[a] This batch of fiberized chips was the source of D, E, and F in Tables I, II, and III.

[b] This batch was used in obtaining the data in Tables V and VI.

[c] This batch was made with a more even chip feed and was used in obtaining the "LL" pulps as in Tables IX and X.

Fiber Liberation

The effect of 6.0% sodium hydroxide at 8.0% consistency was considered by obtaining the data in Table XII. As would be expected from previously described results, the final pH data indicate an excess of alkali was present at the end of each experiment. Yields in the 80-70% range make them of significant potential interest, while screen rejects ranged down to an acceptable 1.4%.

To determine the yield corresponding to when a negligible amount of mechanical force is needed to separate fibers, or that is the fiber liberation point which is a point of demarcation between a semichemical and chemical pulp, the maximum screened yield can be determined as in Fig. 10 using data from Table XII. From this it appears that the relationship between screen rejects, total yield, and screened yield for fibrous products obtained by the procession of steps described reveals a fiber liberation point at a 71-72% total yield that is independent of temperature at least over 40-60°C. This is consistent with the previous discussion, based on Fig. 5 and 6, referring to the indication of there being a fiber liberation point somewhere in the 65-70% yield range. In kraft pulping under optimum conditions of temperature and chip thickness, the fiber liberation point occurs at near 50% yield (6).

Since the defibration point based on the data obtained as in Table XII appears to be independent of temperature, it is of particular interest to determine how temperature may influence other pertinent factors.

TABLE XII

PREPARATION OF EXTRACTED PULPS AT 40-60°C.

I. Alkali Extraction of Fiberized Chips (Lot A)[a]

As for LL-0 plus extensive washing, 93.2%[b] yield (A-1)

II. Chlorine Dioxide Reaction (on A-1)

As for LL-1, 89.5% yield (A-2)

III. Alkali Extractions of A-2

Sodium hydroxide, 6.0%; consistency, 8.0%.

Time, min.	Final pH			Yield, % (Y)			Rejects, %		
	40°C.	50°C.	60°C.	40°C.	50°C.	60°C.	40°C.	50°C.	60°C.
0	--	--	--	89.5	89.5	89.5	∇[c]	x[c]	Δ[c]
5	12.5	12.0	11.9	79.4	76.3	73.8	30.5	16.0	10.6
10	12.4	11.9	11.8	77.2	74.5	71.6	25.7	12.0	6.4
20	12.4	11.9	11.9	76.0	73.7	71.4	16.1	10.1	5.9
40	12.4	11.9	11.8	74.2	72.3	70.5	11.4	4.5	3.0
60	12.2	11.8	11.8	73.4	71.5	70.1	7.9	4.7	--
120	12.1	11.8	11.7	72.3	71.2	69.7	5.5	2.6	--
240	12.1	11.6	11.6	71.8	70.4	69.2	4.2	1.9	1.4
480	--	11.6	--	71.1	69.3	--	2.9	1.4	--

[a] See page 70.

[b] All data on o.d. fiberized chip basis.

[c] See Fig. 14, which is discussed later.

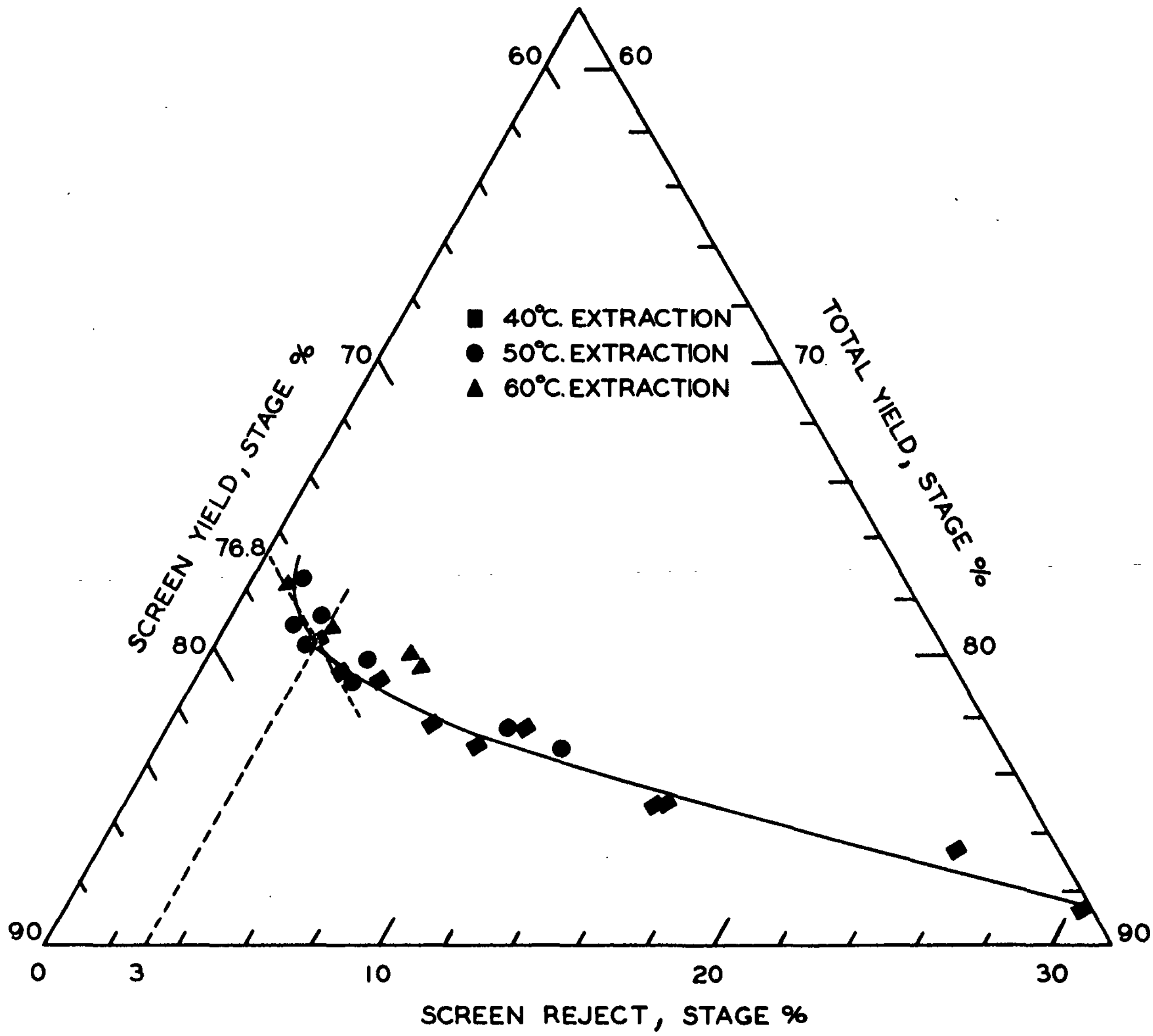

Figure 10. Relationship Between Screen Rejects, Total Yield, and Screened Yield Showing Maximum Screened Yield with 3% Rejects at 71-72% Total Yield (o.d. f.c. Basis)

Rate of Extraction

During caustic extraction, loss in yield is represented by removal of material including carbohydrates plus substance originally present as lignin. Yield as a function of time for three different extraction temperatures is shown in Fig. 11. Extraction rates were determined from these curves and plotted as a function of yield in Fig. 12.

For $-dY/dt = k(Y)$, where

Y = yield,

t = time, and

k = rate constant,

if the extraction rate, $-dY/dt$, is proportional to yield, the reaction would be first order, the curves in Fig. 12 would be straight lines, and one rate constant corresponding to the slope of one line would apply. From Fig. 12 it is obvious that the extraction process is not a simple first-order reaction.

When the initial portion of the process is considered, at 40, 50, and 60°C. the initial extraction rates, $-dY/dt$; were found to be about 47, 105, and 220% per hr., respectively. This means that the initial extraction rate approximately doubled for each 10°C. rise in temperature, indicating that a chemical reaction mechanism is apparently dominating the first part of the extraction process. From Fig. 11, by considering the last portion of the curves, at 40, 50, and 60°C. the extraction rates were found to be approximately 0.22, 0.36, and 0.44% per hour, respectively, or 1/2 to 1/4% of the initial extraction rates. The extraction rates no longer doubled for each 10°C. rise in temperature in the last portion of the caustic extraction, which, therefore, is apparently less temperature dependent than the initial part.

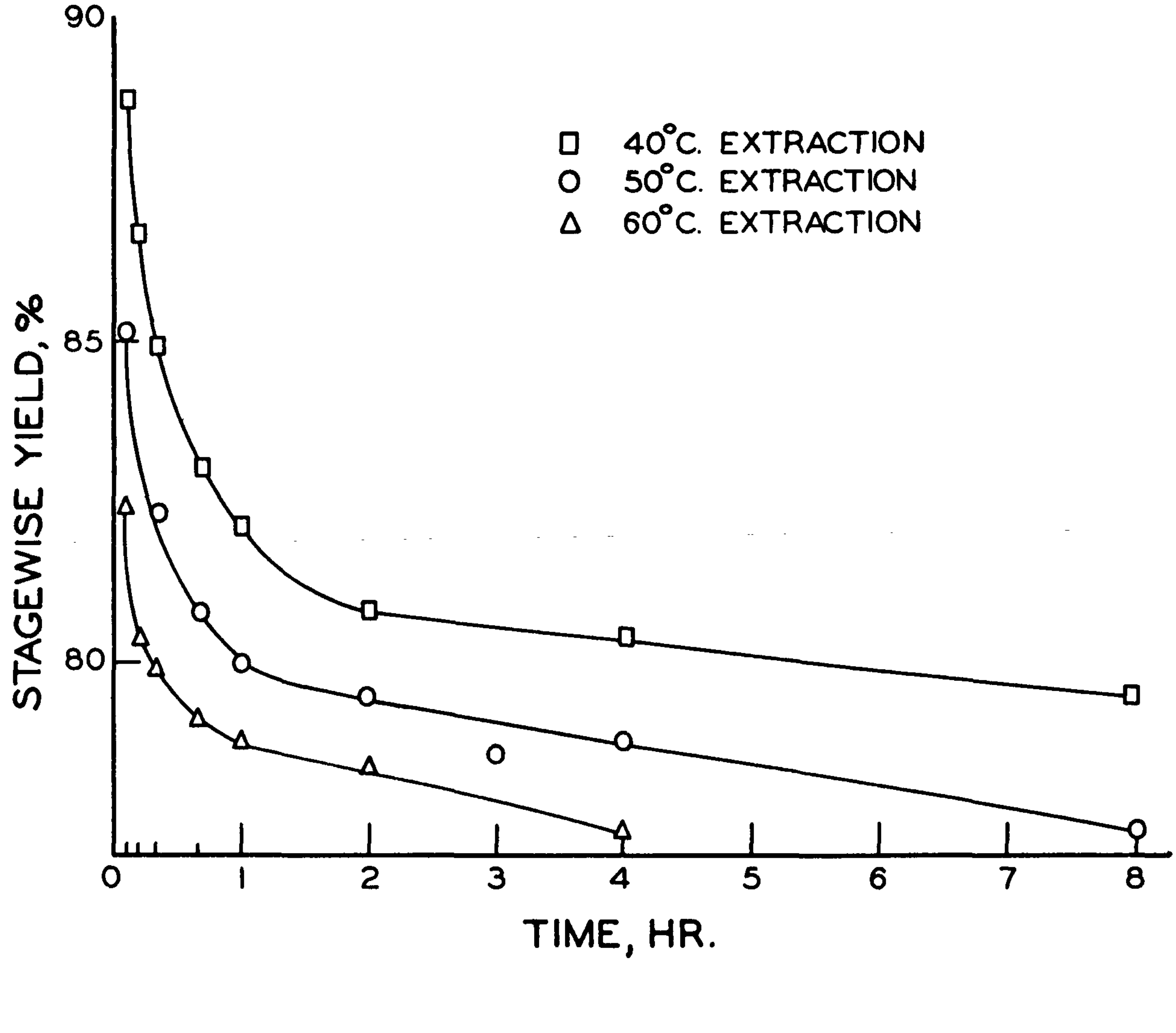

Figure 11. Total Stagewise Yield Versus Extraction Time

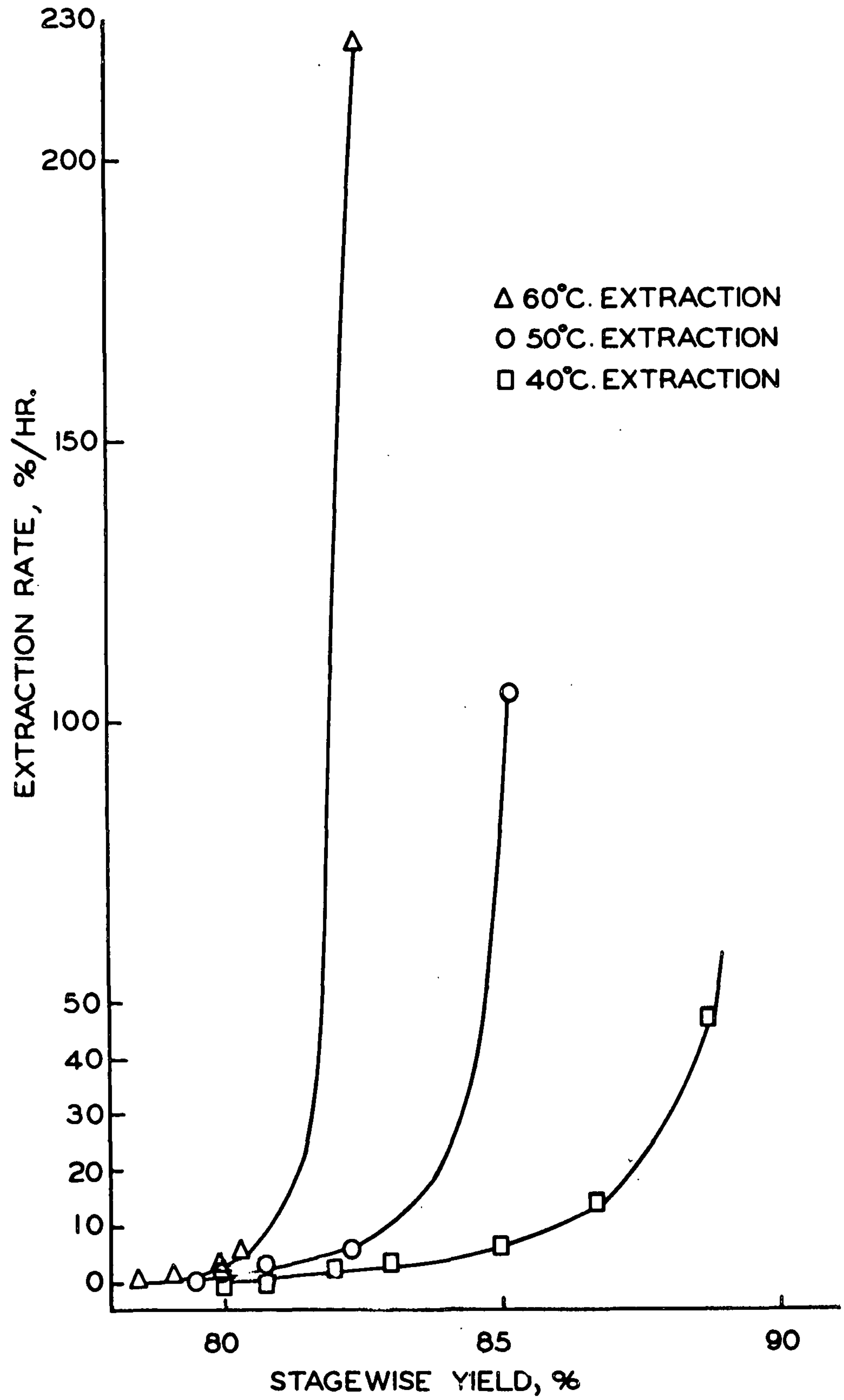

Figure 12. Overall Extraction Rate *Versus* Total Stagewise Yield

To find, if possible, mechanisms of extraction of components with alkali and to obtain information on the chemical composition of the fibrous products of extraction, analyses were obtained as in Tables XIII and XIV. Attempts to use these results to relate chemical, diffusion, or other mechanisms with the removal of identifiable components of the system, essentially left unchanged the nature of the conclusions reached when only yield data were considered as discussed above. How the data in Tables XIII and XIV can be used to reveal what is happening when the alkali extraction is carried out will now be discussed.

Modified Lignin Removal

From Fig. 13, in which the sum of the conventionally determined Klason and acid-soluble lignin content of extracted pulps is plotted against the corresponding sum of acetone-soluble, Klason, and acid-soluble lignin as determined in Buchanan's modified lignin analysis, it can be seen that the latter sum tends to be slightly greater. This is consistent with the observation in Progress Report Four that if fiberized chips are reacted with about 9 and 18% chlorine dioxide there is less lignin unaccounted for by Klason and acid-soluble lignin analyses when a smaller amount of oxidant is used. It is, however, desirable to keep in mind that reaction with 9% chlorine is accompanied by the appearance of a significant amount of material accounted for in the modified lignin analysis as acetone-soluble lignin which is alkali soluble. It is the rate of removal of this material, as seen from the data in Table XIII, that is most influenced by raising the extraction temperature from 40 to 60°C.

TABLE XIII

LIGNIN ANALYSES (O.D. FIBERIZED CHIP BASIS)

A-19, 34, 41, 40 and 37

Code	Table XII Min./°C.	Klason Lignin	Acid Sol.	Total R.L.[a]	Y-RL	Acet. Sol.L.	Klason Lignin	Acid Sol.	Total M.L.[b]	Y-ML
A-2	0	12.3	4.6	16.8	72.7	12.0	4.6	1.6	18.2	71.3
										■[c]
A-21	5/40	8.4	2.5	11.0	68.4	4.9	4.2	1.5	10.6	68.8
A-18	20/40	6.2	1.9	8.1	67.9	3.6	4.0	1.6	9.3	66.7
A-19	40/40	4.9	2.2	7.1	67.1	3.0	3.6	1.4	8.0	66.2
A-33	60/40	5.2	1.5	6.8	66.6	2.8	3.7	1.5	8.0	65.4
A-32	120/40	4.6	1.4	6.0	66.3	1.9	3.3	1.4	6.7	65.6
A-34	240/40	3.7	1.6	5.3	66.5	2.9	3.2	1.2	7.2	64.6
A-31	480/40	4.2	1.1	5.3	65.8	1.9	3.0	1.2	6.1	65.0
										□[c]
A-42	5/60	5.9	1.7	7.6	66.2	2.3	3.8	1.4	7.5	66.3
A-41	10/60	4.4	1.9	6.3	65.3	2.4	3.5	1.4	7.3	64.3
A-39	20/60	4.7	1.4	6.1	65.3	2.0	3.1	2.1	7.6	63.8
A-40	40/60	3.7	1.6	5.3	65.2	1.9	3.2	1.1	6.3	64.2
A-38	60/60	3.9	1.2	5.1	65.0	1.6	2.7	1.2	5.5	64.6
A-37	120/60	3.1	1.4	4.5	65.2	1.2	2.9	1.0	5.1	64.6
A-36	240/60	3.5	1.0	4.5	64.7	1.2	2.7	1.0	4.9	64.3

[a] R.L. = regular lignin analyses.

[b] M.L. = modified lignin analyses.

[c] See Fig. 14, which is discussed later.

TABLE XIV

SUGAR ANALYSES (O.D. F.C. BASIS)

Code	Min.	Gluc.	Xyl.	Man.	Gal.	Arab.	M+Ga+A	Total
A-2	0	47.5	15.3	1.32	0.34	0.23	1.89	64.7
A-2	0	47.2	15.8	1.54	0.52	0.34	2.40	65.4
A-21	5/40°C.	44.3	14.0	1.48	0.37	0.21	2.06	60.4
A-20*	10	44.1	13.4	1.41	0.41	0.28	2.10	59.6
A-18	20	45.4	13.9	1.31	0.29	0.24	1.84	61.1
		45.7[a]	14.5[a]	--	--	--	2.06[a]	62.2[a]
		44.6	13.8	--	--	--	2.00	60.4
A-33	60/40°C.	45.2	13.9	1.43	0.34	0.26	2.03	61.1
A-32	120	44.0	13.2	1.35	0.39	0.27	2.01	59.2
A-34*	240	43.3	12.5	1.50	0.26	0.21	1.97	57.8
A-31	480	41.6	12.0	1.26	0.22	0.16	1.64	55.2
		44.2[b]	13.2[b]	--	--	--	2.00[b]	59.4[b]
A-42	5/60°C.	46.3	14.4	1.38	0.34	0.23	1.95	62.6
A-41*	10	43.7	12.7	1.40	0.13	0.21	1.73	58.1
A-39	20	47.0	14.3	1.50	0.39	0.25	2.14	63.4
		46.3[a]	14.5[a]	--	--	--	2.02[a]	62.8[a]
		44.3	13.8	--	--	--	1.94	60.0
A-40*	40/60°C.	42.6	11.9	1.23	0.18	0.14	1.55	56.1
A-38*	60	43.4	12.8	1.40	0.25	0.21	1.86	58.1
A-37*	120	44.1	12.9	1.40	0.33	0.23	1.96	59.0
A-36	240	43.1	12.7	1.30	0.26	0.18	1.74	57.5
		43.5[c]	12.8[c]	--	--	--	1.85[c]	58.2[c]

[a] Mean, including duplicate analyses at 0 minutes.

[b] Excluding value at 480 minutes.

[c] Excluding value at 40 minutes.

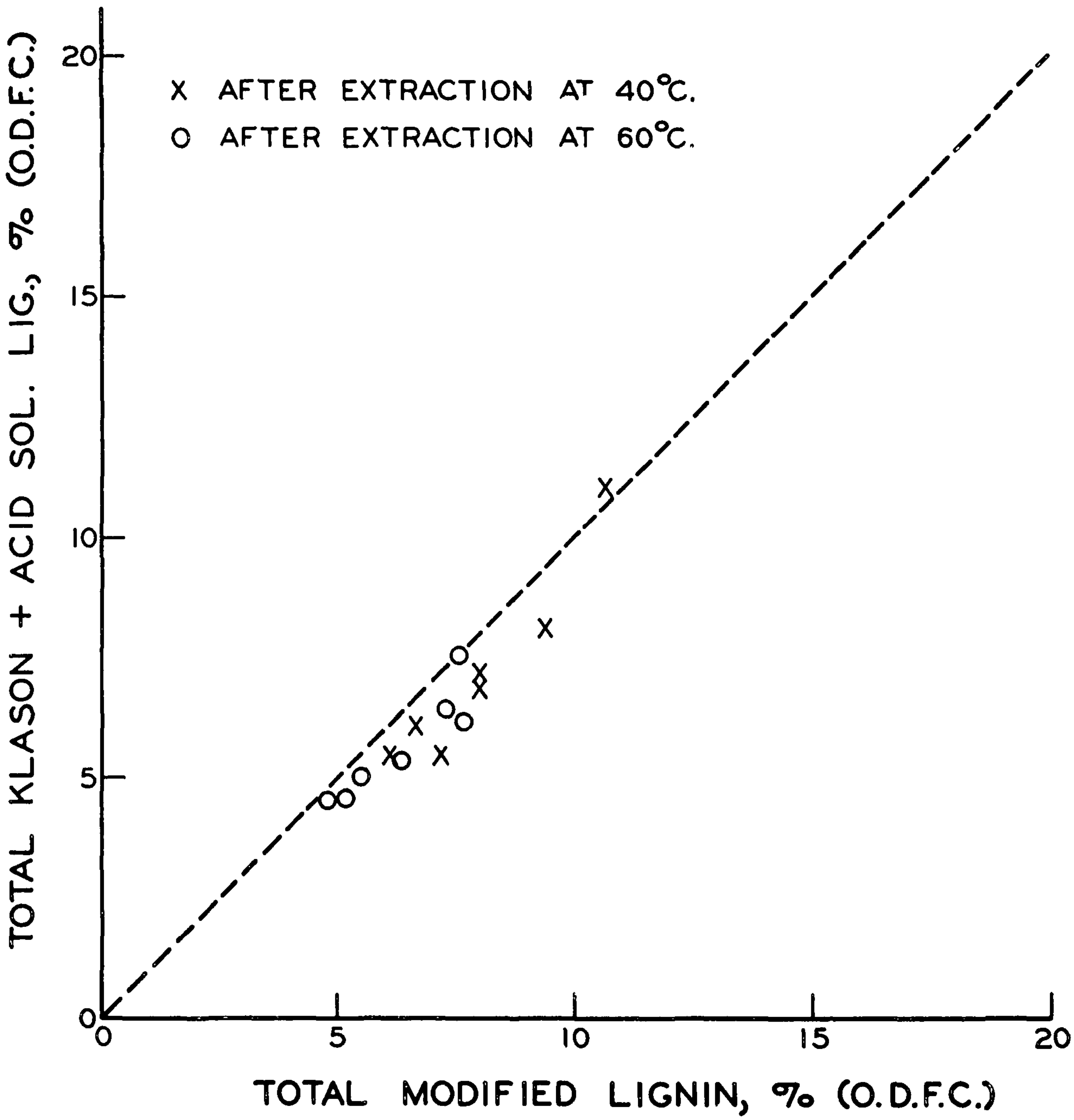

Figure 13. Comparison of the Sum of Klason Plus Acid-Soluble Lignin and Total Modified Lignin, the Curve Being Drawn with $y = x$

The differences shown in Table XII for yields obtained at 40 compared with 60°C. for each extraction time when converted to a total modified lignin-free basis, Y - M.L. (Table XIII), are noticeably reduced. This is represented graphically in Fig. 14 which shows that extraction at 60 instead of 40°C. favors more rapid and more complete removal of total modified lignin, accompanied by greater separation into fibers as reflected by a decrease in screen rejects.

Yield minus modified lignin content, after extraction for approximately an hour, tends to become constant at a level apparently 1 or 2% greater at 40 compared with 60°C. (Fig. 14), indicating there may be some loss of carbohydrates as a consequence of using the higher temperature. To learn more about this question, the sugar analyses in Table XIV may be considered.

Carbohydrate Retention

Consideration of the sugar analyses on the basis presented in Table XV indicated changing the extraction temperature from 40 to 60°C. had no effect. This was confirmed by statistical analysis in that there is no significant difference (0.05 level) between the set of analyses obtained after the 40°C. extraction for 5, 10, 20, 60, 120, and 240 min. and the corresponding set obtained after the 60°C. extraction. In view of the apparent advantage of using the higher temperature to decrease total modified lignin content, the observation that raising the temperature from 40 to 60°C. causes no depletion in polysaccharide content is significant.

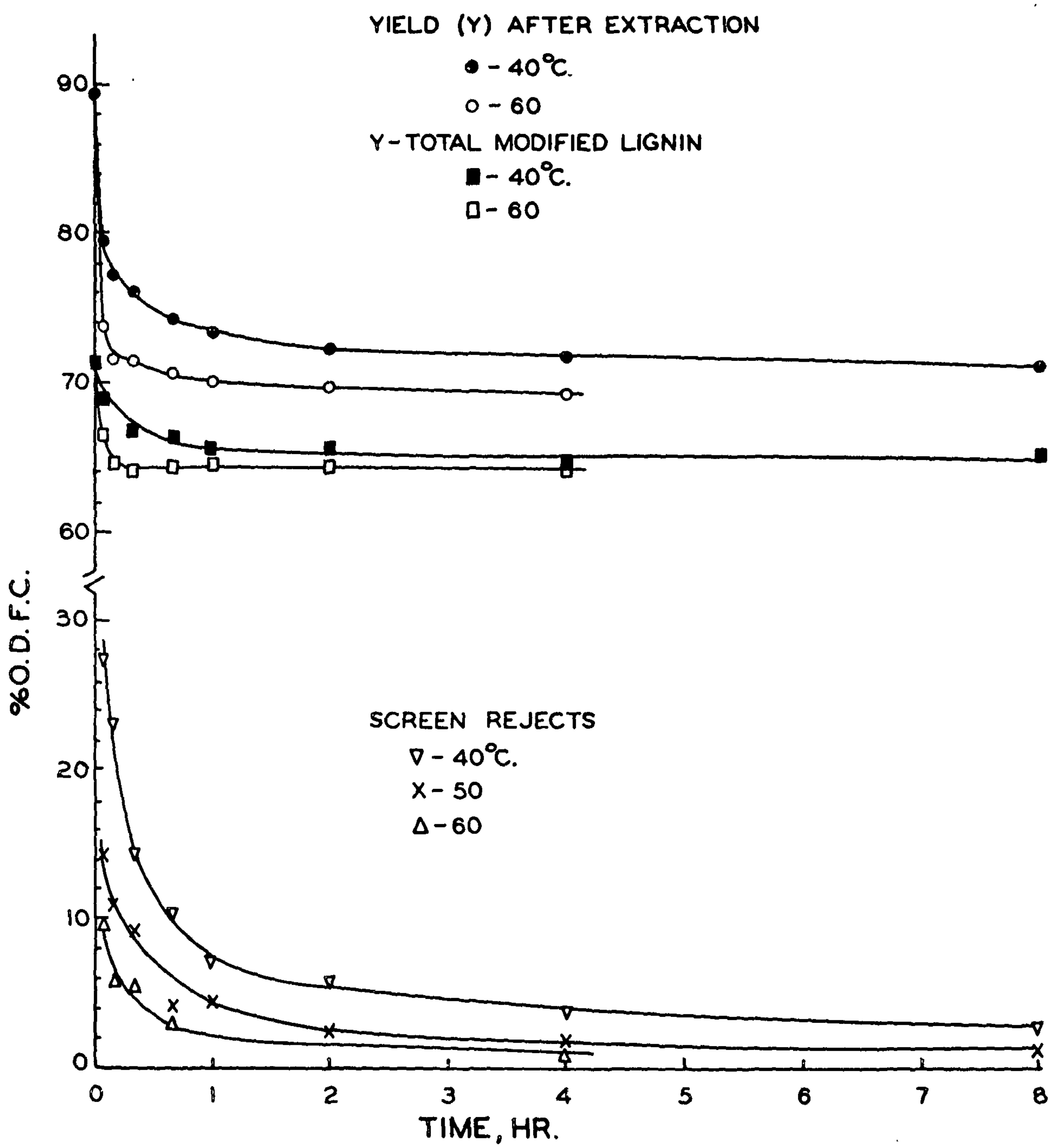

Figure 14. Relationships Showing the Influence of Time on Yield, Yield Minus Total Modified Lignin Content, and Screen Rejects at the Noted Temperatures

TABLE XV

SUGAR ANALYSIS MEANS/TIME/TEMP.

Min.	Glucose 40° - 60°C.	Xylose 40° - 60°C.	Mannose-Galactose-Arabinose 40° - 60°C.	Total 40° - 60°C.
0 (A-2)	47.3	15.5	2.1	64.9
0-20[a]	45.7-46.3	14.5-14.5	2.1-2.0	62.3-62.8
5-20[b]	44.6-44.3	13.8-13.8	2.0-1.9	60.4-60.0
60-240[c]	44.2-43.5	13.2-12.8	2.0-1.9	59.4-58.2

[a] Mean for 0, 5, 10, and 20-min. caustic extractions.

[b] Mean for 5, 10, and 20-min. caustic extractions.

[c] Mean for 60, 120, and 240-min. caustic extractions.

Note: The data represent the means derived from individual sugar analyses as shown in Table XIV.

In addition, statistical analysis confirmed that time of alkali extraction has a positive effect (0.05 level) on the polysaccharide component as reflected by the sugar analyses. The mean value of the total sugar content for each extraction time common to the 40 and 60°C. temperatures used is plotted against time in Fig. 15. This includes intervals applicable to the ordinate that reflect experimental and analytical variability to define the limits within which the true total sugar value would fall at the 95% confidence level. The decrease in total sugars with time of extraction occurs without there being a similar decrease in yield minus total modified lignin, as in Fig. 14. Thus, it appears possible that with increased time of extraction, changes in the saccharide units of the polysaccharides are occurring without there being a parallel degree of detachment of the changed groups. In addition, the data indicate that these observations made with respect to total sugars also apply if either glucose or xylose (the main polysaccharide hydrolysis products) are considered separately.

When considering the carbohydrate portion of the products obtained after caustic extraction, it is desirable not only to study possible changes in the polysaccharides as revealed by sugar analyses, but also other components such as uronic acids and acetyl groups that could be removed. Some analyses concerning considerations of this type are included in Table XVI.

From the A-coded data it is apparent that alkali extraction for 5, 60, and 480 min. at 40°C. was accompanied by progressively greater removal of acetyl groups. It can also be seen that the acetyl contents of the products A-2 and LL-2 are significantly different in spite of the fact that these products were obtained by a nominally identical procedure. While the reason is unknown, it could be associated with a variation in the two lots of chips used. In the same connection, it is noted that the yields are consistently lower for Pulps LL-10, LL-60, and LL-240 when

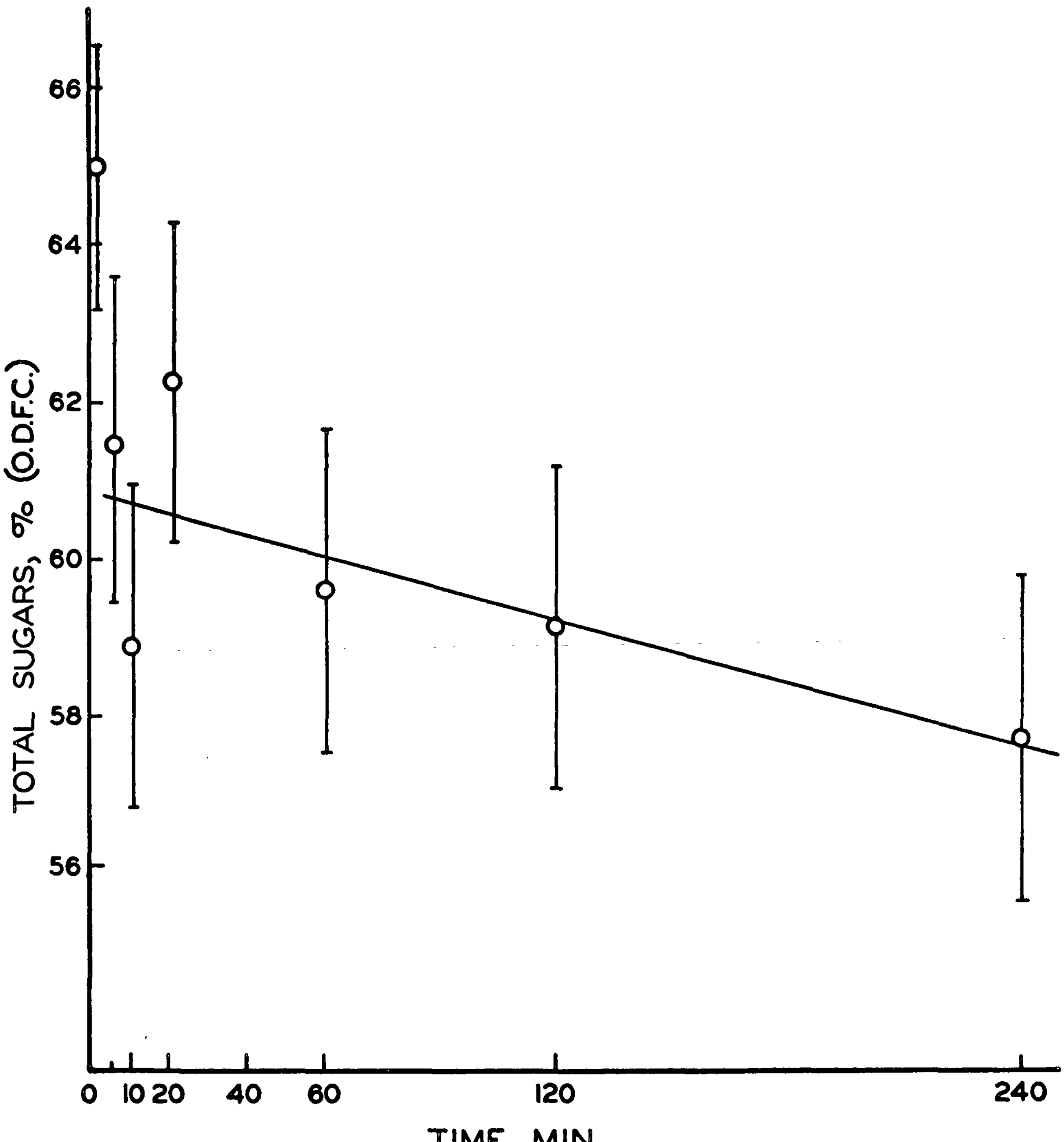

Figure 15. Relationship Between Sugar Content and Time of Extraction with Alkali After Reaction with Chlorine Dioxide

TABLE XVI

MISCELLANEOUS ANALYSES (O.D. FIBERIZED CHIP BASIS)

Code	Min./°C. (Alkali)	Polyur., %	*Acetyl, %	Glucose, %	Xylose, %	M+G+A, %	*Mod. Lig., %	Total, %	Yield, %
A-2	-	4.7	1.2	{47.5 47.2	{15.3 15.8	{1.9 2.4	18.2	89.0	89.5
A-21	5/40	3.3	0.4	44.3	14.0	2.1	10.6	74.7	79.4
A-33	60/40	2.6	0.2	45.2	13.9	2.0	8.0	71.9	73.4
A-31	480/40	2.1	0.1	41.6	12.0	1.6	6.1	63.5	71.1
LL-0	-	4.4	3.8	42.4	17.6	2.8	25.0	96.0	100
LL-2	-	5.8	3.4	43.3	17.0	2.2	17.2	88.9	90.7
LL-10	10/50	2.3	0.2	41.4	13.8	2.0 est.	9.6	69.3	73.0
LL-60	60/50	2.5	0.1	38.6	12.8	1.6	7.0	62.6	69.0
LL-240	240/50	2.2	0.1	39.3	12.1	1.6	6.9	62.2	67.6

* [illegible]

compared with the yields of 74.5, 71.5, and 70.4%, respectively, for similarly prepared products (Table XII). Apparently, this is a reflection of the chips used for the latter having a lower polysaccharide content, as revealed by the sugar analyses.

These were all determined by ion-exchange chromatography. Four samples were also analyzed by both gas and paper chromatography, the various results being presented in Table XVII. Although for each method of sugar determination the calculation took hydration increase and hydrolysis loss into account, the total sugars analyses by the ion-exchange method are significantly lower, probably about 5%.

TABLE XVII

SUGAR ANALYSIS BASED ON DIFFERENT METHODS

Code	Total Sugars (G + X + Ga + A + M) Gas	Paper	Ion Exchange
A-34	63.6	65.2	57.8
A-37	61.9	61.2	59.0
LL-10	63.5	62.1	57.2
LL-60	59.5*	60.9*	53.0

Further Consideration of Lignin Removal by Alkali

In the foregoing discussion on caustic extraction after chlorine dioxide reaction, the influence of extraction time on handsheet data, fiber liberation, rate of extraction, modified lignin removal, and retained carbohydrates were all considered on the basis of extracting with 6.0% sodium hydroxide at an 8% consistency. While polysaccharides were apparently more influenced by time than temperature, since lignin removal is favored by a temperature of 60 compared with 40°C., an obvious question is whether even greater removal of modified lignin could be achieved by extracting at a higher consistency. For the same amount of added alkali this would mean less water to heat, a more concentrated effluent, and a higher concentration of alkali. Alternatively, less alkali would need to be added to provide the same initial concentration and inspection of the final pH data in Table XII indicates this is a possibility.

To study the influence of extraction at a consistency of 12%, for example, the bulky, incompressible character of fiberized chips presents a practical problem concerned with good mixing and contact between the liquor and fiberized chips. This was overcome by further fiber separation in a PFI mill before extraction. It was found, as described in the experimental part, that material was dissolved when shives were removed by screening. Shive removal provided a more uniform product with which to work.

In Table XVIII, data on the fibrous material before and after further fiber separation are presented. When preparing the disintegrated fibrous material, about 3.0% was dissolved in water, and it is of interest to note a corresponding loss in Klason lignin. The material dissolved apparently represents partially modified lignin unable to be removed readily by water through the existing porous structure of the fiberized chips before further disintegration. Entry of small molecules into the cell wall of a fiber and the size of macromolecules which can diffuse out of the wall are obviously important in pulping by selective delignification, and some recent work (7) has led to the suggestion that in kraft and sulfite pulping, while at first the pores are small, as delignification proceeds larger molecules may leave the cell wall. However, the observation (supported by the data in Table XVIII) that a lignin fraction was dissolved when fiberized chips were further disintegrated is regarded for the time being as a side result of studying alkali extraction at higher consistency.

TABLE XVIII

DATA ON A-2 (TABLE XII) BEFORE AND AFTER FURTHER FIBER SEPARATION

	Undisintegrated	Disintegrated
Yield, %	89.5[a]	86.4
Total Klason + acid-sol. lignin	16.8	13.7
Klason lignin	12.4	9.1
Acid-sol. lignin	4.6	4.6
Total modified lignin	18.2	13.4
Acetone-sol. lignin	12.0	4.9
Klason lignin	4.6	5.1
Acid-sol. lignin	1.6	3.4

[a] All percentages on o.d. fiberized chip basis.

Data in Table XIX reveal that the yields of extracted products after subtraction of Klason plus acid-soluble lignin content tended to reach a common minimum yield of 65-66% (Y-RL), which is the same as that found previously (Table XIII) when using a lower consistency. Thus, the higher alkali concentration when extraction was carried out with 6% sodium hydroxide at 12 instead of 8% consistency appears to have resulted in the same degree of carbohydrate retention.

When the amount of Klason lignin plus acid-soluble lignin retained after extraction is considered on the basis depicted in Fig. 16. it is obvious that lignin content is rapidly reduced in the first part of the extraction, then tends to level off at a value related to the extraction conditions, as was observed previously.

TABLE XIX

DATA ON PRODUCTS OF ALKALI EXTRACTION OF PFI-MILLED PULP A-2

	40°C.								60°C.											
	4% NaOH		6% NaOH						4% NaOH						6% NaOH					
Time, min.	Yield	pH	Yield	pH	Klason Lignin	Acid-Sol. Lignin	Regular Lignin	Yield-Regular Lignin	Yield	pH	Klason Lignin	Acid-Sol. Lignin	Regular Lignin	Yield-Regular Lignin	Yield	pH	Klason Lignin	Acid-Sol. Lignin	Regular Lignin	Yield-Regular Lignin
									Consistency 12%											
0	86.4	--	86.4	--	9.1	4.6	13.7	72.8	86.4	--	9.1	4.6	13.7	72.8	86.4	--	9.1	4.6	13.7	72.8
5	--	--	74.9	12.5	5.4	2.5	7.9	67.0	--	--	--	--	--	--	72.7	12.1	4.7	2.0	6.7	66.0
10	76.4	12.0	73.1	12.5	--	--	--	--	73.1	11.6	4.9	2.0	6.9	66.2	71.5	12.0	4.2	1.7	5.9	65.6
20	73.7	12.0	72.1	12.2	4.2	2.0	6.2	65.9	72.3	11.6	4.3	1.7	6.0	66.3	70.7	12.1	3.7	1.7	5.4	65.3
40	73.7	11.9	71.6	12.4	4.0	1.8	5.8	65.8	71.7	11.9	4.2	1.7	5.9	65.8	70.5	12.2	3.2	1.5	4.7	65.8
60	73.1	11.9	70.7	12.6	3.5	1.7	5.2	65.5	71.3	11.6	3.9	1.6	5.5	65.8	69.7	12.0	3.4	1.6	5.0	64.7
120	74.4	11.9	70.4	12.6	3.3	1.6	4.9	65.5	70.4	11.5	3.5	1.4	4.9	65.5	69.6	12.1	3.0	1.4	4.4	65.2
240	--	--	69.7	12.2	--	--	--	--	70.2	11.3	3.3	1.3	4.6	65.6	68.9	12.0	2.7	1.4	4.0	64.9
480	--	--	69.7	12.2	--	--	--	--	69.9	11.4	--	--	--	--	--	--	--	--	--	--
									Consistency 8.0%											
5	--	--	--	--	--	--	--	--	--	--	--	--	--	--	72.1	--	4.6	1.9	6.5	65.6
10	--	--	75.2	12.4	--	--	--	--	--	--	--	--	--	--	71.4	11.9	4.1	1.7	5.7	65.7
20	--	--	76.4	12.4	--	--	--	--	--	--	--	--	--	--	70.3	12.0	3.6	1.6	5.2	65.1
40	--	--	73.1	12.3	--	--	--	--	--	--	--	--	--	--	70.6	11.9	3.2	1.4	4.7	65.9
60	--	--	73.1	12.3	--	--	--	--	--	--	--	--	--	--	69.7	11.9	3.0	1.4	4.4	65.3
120	--	--	--	--	--	--	--	--	--	--	--	--	--	--	69.1	11.9	3.1	1.3	4.5	64.6

Note: All data on ovendry fiberized chip basis. "Regular" lignin denotes Klason plus acid-soluble lignin.

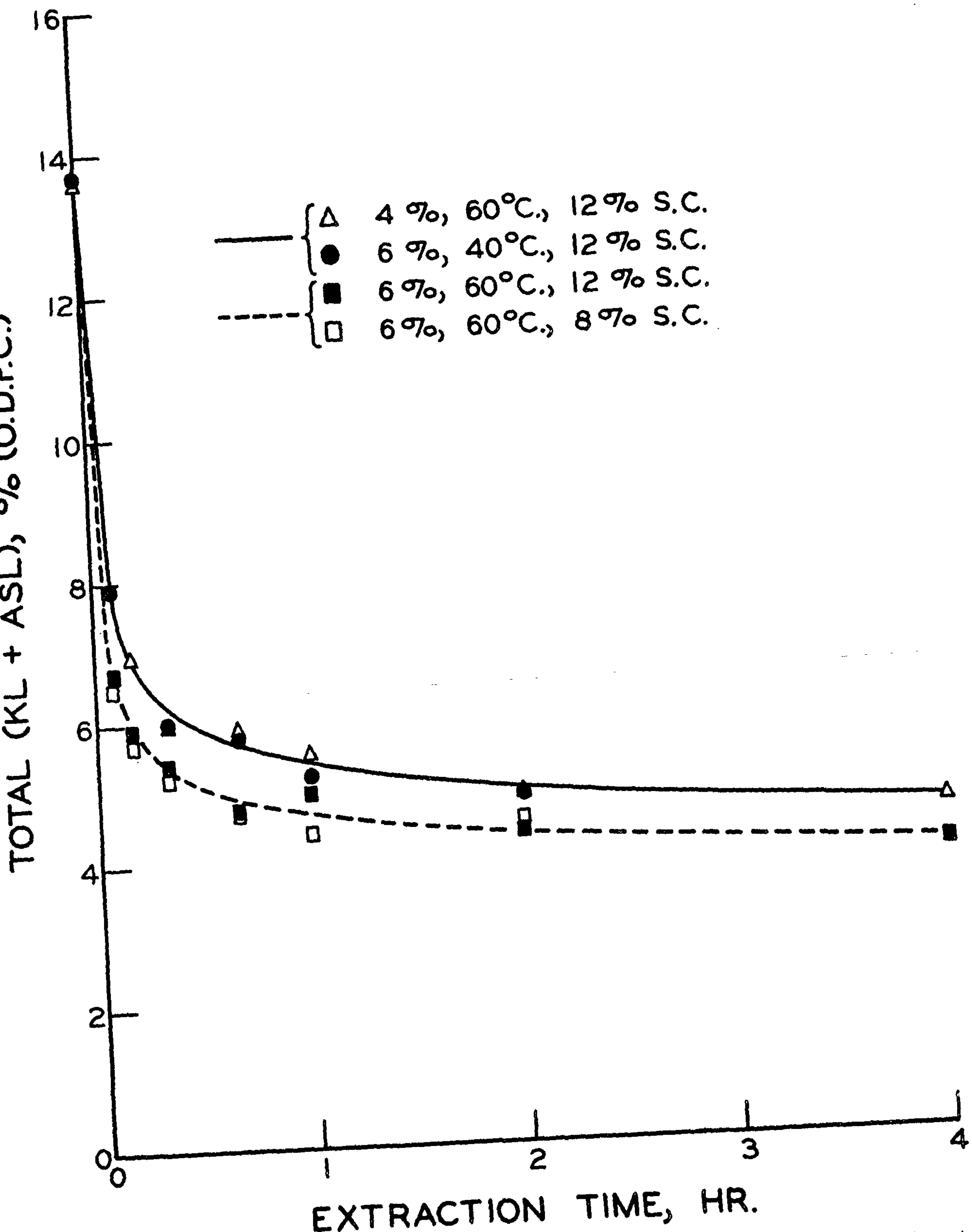

Figure 16. Klason Lignin Plus Acid-Soluble Lignin Retained After Alkali Extraction at 12 and 8% Consistency of PFI-Milled Fiberized Chips

The data for extraction at 60°C. with 4% sodium hydroxide and at 40°C. with 6% sodium hydroxide fortuitously fall on the upper curve. By using 6 instead of 4% sodium hydroxide at 60°C., the lignin content levels off at a value about 1% lower.

Lignin content is shown in Fig. 17 as a function of extraction time, temperature, and consistency when 6.0% sodium hydroxide is used. At the higher consistency, for which a PFI-milled material was used, lignin content was lowest by about 0.5%. By obtaining data, included in Table XIX, at 8% consistency on PFI-milled material it appears the lowest lignin content arises from further fiberization rather than from use of a higher consistency.

In summary, caustic extraction at higher consistency after further fiberization apparently provides the same degree of carbohydrate retention, a definite small decrease in lignin content, and potential advantages from processing a more fiberized material.

EXPERIMENTAL

Raw Materials

Two lots of aspen chips were used. Lot A3/55 was used in obtaining the data in Tables IX-XI. The Bauer-McNett classification of the fiberized product is recorded in Table XI.

The A-coded data in Tables XII-XV and the associated figures are based on the use of a grab sample of aspen chips.

Delignification with Aqueous Chlorine Dioxide and Alkali

For the LL-coded pulps the same procedures were followed as described on page 42, except where noted in the tables.

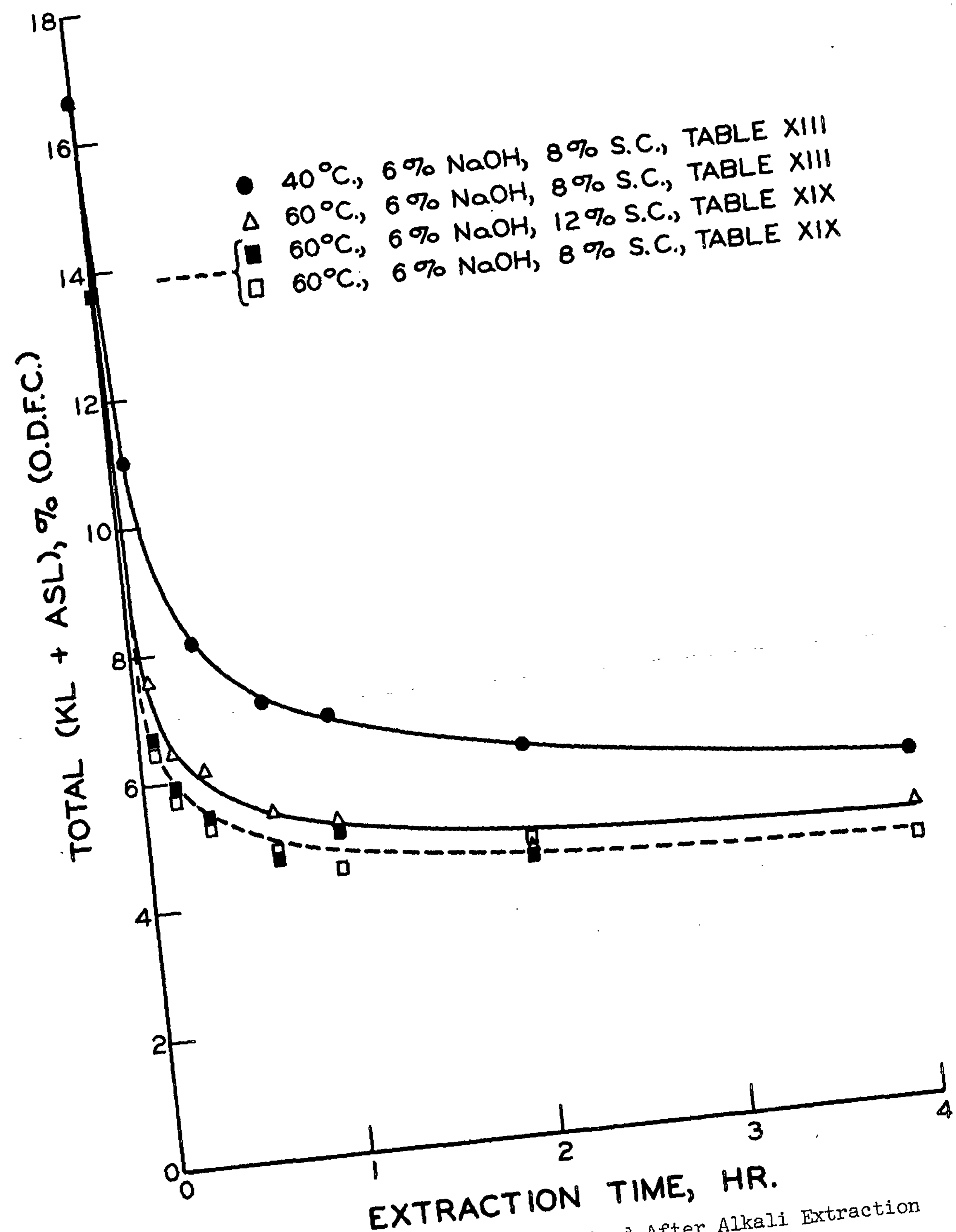

Figure 17. Comparison of Lignin Retained After Alkali Extraction Under Different Conditions

For the data obtained in Table XII, after alkali extraction, the fiberized chips were washed with several changes of tap water; the washed fiber was treated with approximately 1% by weight acetic acid at less than 6% consistency for 1 hr. The fiberized chips were then collected, washed with several changes of tap water, dewatered in a centrifuge, and shredded to facilitate uniform sampling; o.d.content, 39.2%.

For the reaction with chlorine dioxide, the alkali buffer solution was added to the aqueous chlorine dioxide just before mixing with the fiberized chips. The reaction product was washed with several changes of tap water, shredded, approximately 0.1% formaldehyde added as a preservative, and the product placed in cold storage for use as required.

In the alkali extractions after reaction with chlorine dioxide, distilled water was used throughout. After washing with several changes of water, the pulp was soaked in dilute acetic acid (3% o.d. fiberized chips) for an hour, collected, thoroughly washed, and dewatered.

Handsheet Preparation and Testing

The pulps obtained as in Table X were screened on a 0.006-in. flat screen, beaten in a Valley beater essentially in accordance with TAPPI Standard Method T 200 ts-66 with handsheet preparation and testing carried out by the methods defined above.

Lignin Analyses

Modified lignin analyses were carried out as described in Report Two, except for the change in the Klason lignin procedure noted below.

Klason lignin analyses were determined according to Institute Method 428 (which is essentially a modification of TAPPI Standard Method T 222) except that the precipitate was collected on glass fiber filters instead of in crucibles (8).

Acid-soluble lignin analyses were determined as follows. All of the Klason lignin filtrate was diluted to 1.0 liter and the absorptivity determined at 208 nm. (using matched silica cells) against a sulfuric acid standard made by diluting 10 ml. of 72% sulfuric acid to 1.0 liter. If necessary, the filtrate was further diluted. Taking the dilution factor into account, the amount of acid-soluble lignin was calculated using an absorptivity value of 105 (9).

Sugar Analyses

Gas chromatographic analyses were carried out by a modified method based on that of Crowell and Burnett (10).

Paper chromatographic analyses were carried out according to the method of Saeman, *et al*. (11).

Ion-exchange chromatographic analyses were carried out according to the method of Kesler (12).

Polyuronides and Acetyl Determination

Institute Method 25 was used for the determination of polyuronides.

Acetyl content was determined by the method of Whistler and Jeanes (13).

Further Separation of Fiberized Chips After Chlorine Dioxide Reaction

Fiberized chips after reaction with chlorine dioxide as in Table XII were further separated at 25% consistency for 1 min. in a PFI mill with a 3.4-kg. load.

Screening the product on a 0.012-in. flat screen removed the coarsest material (2.8% on o.d. pulp basis), the accepts being used for experiments to obtain the data in Table XIX.

To determine material loss, a weighed sample of fiberized chips after reaction with chlorine dioxide was disintegrated (3 min.) at approximately 2% consistency in a Waring Blendor, collected in a sintered-glass filter, disintegrated again (3 min., at approximately 2% consistency), and filtered. A part of the combined filtrates was evaporated to dryness and another part filtered on a finer sintered-glass filter to remove fines. Found: water solubles - 3.1% (o.d. f.c. basis). Yield of PFI-milled fiberized chips after PFI milling - 86.4% (o.d. f.c. basis).

BLEACHING

DISCUSSION

Exploratory Experiments

The studies already described left unanswered questions concerning how unbleached pulp brightness could be increased and whether bleaching could be achieved without substantial loss of yield.

Logically, chlorine dioxide is the first chemical to consider. As demonstrated by the data included in Table XX, neither chlorine dioxide nor alkaline peroxide provided a satisfactory gain in brightness. On the other hand, experiments with hypochlorite succeeded in revealing a brightness of 80 GE could be reached in one stage. This finding indicates a higher brightness would be achieved by a chlorination-alkali extraction-hypochlorite bleaching sequence by implication of what is known about bleaching chemical pulps, which has been assumed to be applicable for the time being.

Hypochlorite Bleaching and Handsheet Data

Following the experiments that led to the results set out in Table XX, to obtain enough pulp for handsheet preparation approximately equal amounts of Pulps LL-60 and LL-240 (Table X) were combined, then bleached with hypochlorite to 80-82 GE brightness as recorded in Table XXI. Although the unbleached pulp had been screened, the bleached yield of 65.5% was calculated assuming that if the rejects had been left in, the percentage loss on bleaching would have been the same for screened or unscreened pulp. Thus, a one-stage bleach with hypochlorite provides about 30 points gain in brightness to near 80 GE without a loss in yield, indicative of significant sacrifice of carbohydrates during lignin removal.

TABLE XX

EXPLORATORY BLEACHING EXPERIMENTS

Consistency, 12.0%[a]

	LL-10[b]			LL-60[b]					LL-240[b]		
A. Chlorine dioxide, %	--	0.5		1.0		1.5	0.5		1.0		1.5
Temp., °C.: start/2 hr.	--			40/60					40/60		
Final pH	--	3.8		3.7		3.3	3.7		3.5		3.1
Time, min. (starch/I⁻)	--	50		80		150	60		93		190
Brightness, GE	--	62.5		67.0		69.0	63.0		68.5		69.0
Heat-aged, GE	--	59.0		62.5		64.0	60.0		64.5		65.0
B. Peroxide[c], % (3.25 hr.)	--	0.5		1.0		1.5	0.5		1.0		1.5
Temp., °C.	--			50					50		
Final pH	--	9.3		9.5		9.6	9.4		9.7		9.8
Resid. perox., %	--	0.1		0.4		0.6	0.1		0.4		0.6
Yield, % o.d. pulp	--	99		99		99	98		99		98
Brightness, GE	--	55.0		60.0		62.0	53.5		58.5		60.0
Heat-aged GE	--	54.0		58.0		61.0	52.5		57.5		59.0
C. Hypochlorite, % av. Cl_2	3.5	1.5	1.5	3.5	3.5	5.5	1.5	1.5	3.5	3.5	5.5
Temp., °C.	40			40					40		
Sodium hydroxide, %	1.2	0.9	0.9	1.7	1.2	3.4	0.9	0.9	1.7	1.2	3.4
Initial pH	10.9	10.4	10.4	10.8	10.9	11.2	10.4	11.0	10.9	10.9	11.2
Final pH	8.2	8.4	8.2	8.2	8.3[d]	8.0	8.5	8.2	7.9	8.3[d]	8.1
Time, min. (starch/I⁻)	120	110	120	180	150[d]	250	120	120	175	150[d]	260
Brightness, GE	--	74.5	--	80.0	--	80.5	75.5	--	79.0	--	82.0
Heat-aged GE	--	69.5	--	74.0	--	75.0	71.0	--	74.0	--	76.5
Canadian freeness[e]	410	--	380	--	250	--	--	360	--	240	--

[a] All percentage data on o.d. fiberized chip basis.

[b] Screened pulps LL-10, LL-60 (Kappa no., 22.6), and LL-240 (Kappa no., 20.0) were obtained in 73.0, 69.0, and 67.6% yield, respectively, as detailed elsewhere.

[c] Plus 5% 40-42°Bé. (o.d. pulp). The peroxide solution included 0.5 g. Epsom salts/ℓ., ca. 9-12 g. H_2O_2/ℓ., and 0.125 g. NaOH/g. H_2O_2.

[d] Time limited.

[e] After 500 counts in British disintegrator.

TABLE XXI

BLEACHING PULP LL-60 + LL-240: HANDSHEET PROPERTIES

Bleaching Data

Hypochlorite, %[a] available Cl_2	3.5	Consistency, %	12
Sodium hydroxide, %	1.2	Temp., °C.	40
Initial pH	11.0	Time, min.	150
Final pH	8.5	Yield, %	65.5
Brightness, GE	80.0, 82.0[b]	Heat-aged GE	73.0, 78.0[b]

Handsheet Data

Canadian freeness	240[c]	175[d]
Density, g./cc.	0.743	0.753
Opacity, %	68.1	66.7
Breaking length, km.	8.92	9.00
Burst factor, TAPPI	50.8	53.5
Tear, TAPPI	65.4	60.2
Zero-span breaking length, km.[e]	18.1	18.4

[a] All percentage data are on an o.d. fiberized chip basis

[b] Sulfurous acid-washed pulp.

[c] After circulation for 5 min. in Valley beater with no bedplate load.

[d] As for [c] plus 1200 rev. counts in British disintegrator.

[e] Handsheets had basis weight 52-51 g./m.^{2} (o.d.) and contained fiber bundles.

The handsheet data in Table XXI reveal that hypochlorite bleaching has led to an unusual situation where the relatively unbeaten bleached pulp is more like the corresponding unbleached pulp after beating compared with before beating (compare Table X) with respect to freeness, sheet density, and breaking length. On the other hand, the tearing strength is more like that of the unbeaten, unbleached pulps, and the zero-span breaking length is at least equal to the maximum achieved for the unbeaten pulp. There is some evidence in Table XX indicating time of exposure of the pulp to alkali is a factor influencing freeness after bleaching, and perhaps it is too soon to decide from the data in Table XXI whether hypochlorite-bleached pulps prepared via reaction with aqueous chlorine dioxide are hydrodynamically unstable.

MICROSCOPIC EXAMINATION OF FIBERS

DISCUSSION

Unbleached and Hypochlorite-Bleached Fibers

For an unbleached pulp such as LL-60, Fig. 18 illustrates that bleaching with hypochlorite enhances the degree of separation into individual fibers without any apparent increase in the amount of fines and cell-wall debris.

When these fibers were treated with "C" stain, an expected overall differ ence in color was noted in that the bleached pulp (Table XXI) was significantly mor blue. However, there were other differences. In the unbleached pulp, the vesse] elements were stained a yellow brown, some individual fibers were already staining blue, the fiber bundles as in the upper portion of Fig. 18 had about the same colo as the vessel elements, and sometimes there was seen a pink-stained, well-defined tertiary wall or gelatinous "G"-layer that was highly birefringent when examined under polarized light. The occurrence of this "G"-layer has been described previously (14), and similarly stained tertiary wall was observed in the bleached pu This differed from the unbleached pulp in that the vessel elements were stained t indicating there was now less lignin present. While most fibers were a blue co] some were stained a yellow brown, especially those not yet completely separated individual fibers, as seen in the lower part of Fig. 18. Examination of a blea pulp sample stained with Crystal Violet and Erythrosin B (which turns nonlignifi walls pink and lignified walls violet) also revealed lignin remaining in bundles fibers and in addition an occasional vessel showed some lignin present.

Thus, although a single-stage hypochlorite bleach enhances the degree separation into individual fibers and is effective in raising brightness to abc

Figure 18. Unbeaten, Screened Pulp Before and After Bleaching, Illustrating Greater Separation into Individual Fibers in the Bleached Pulp. Graff's "C" Stain Mount; Magnification 35X

80 GE, optimum results were not being obtained since some of the wood elements were incompletely delignified.

Outer Walls of Pulp Fibers and Fiber Damage

Some of the questions that arise when this pulping process is considered concern matters such as: (a) whether significant changes occur in the fiber at some stage in the process, (b) whether the primary or some part of the secondary wall is left exposed in the pulp, and (c) whether significant damage occurred during chip fiberization. There is an extensive literature on fiber studies, and without attempting to review this, some consideration has been given to the kind of question raised above.

The influence of alkali extraction on fiber morphology and sheet properties was noted in Report Three, in which Fig. 15 revealed partial delamination of the cell walls; and Fig. 17 compared with Fig. 16 showed a significant change in the general appearance of beaten fibers after alkali extraction.

When Victoria Blue-stained, unbeaten, bleached pulp (Table XXI) was examined, it was again possible to see fibers in which delamination or wall separation had occurred, as shown in the upper half of Fig. 19. If fibers stained with Victoria Blue are subjected to swelling in cuprammonium solution, differences in the nature of the outer wall of the fibers become more apparent--for example, as in the lower half of Fig. 19. On the right side can be seen a fiber in which the S_2 layer or main secondary wall has been able to swell without restraint in the cuprammonium solution and appears as a wide, irregularly outlined band through which the swelling-resistance "G"-layer or tertiary wall appears to zigzag. It has been stated by Bucher (15) that the tertiary wall, which is hard to swell, is of importance to the stability, elasticity, and flexibility of fibers.

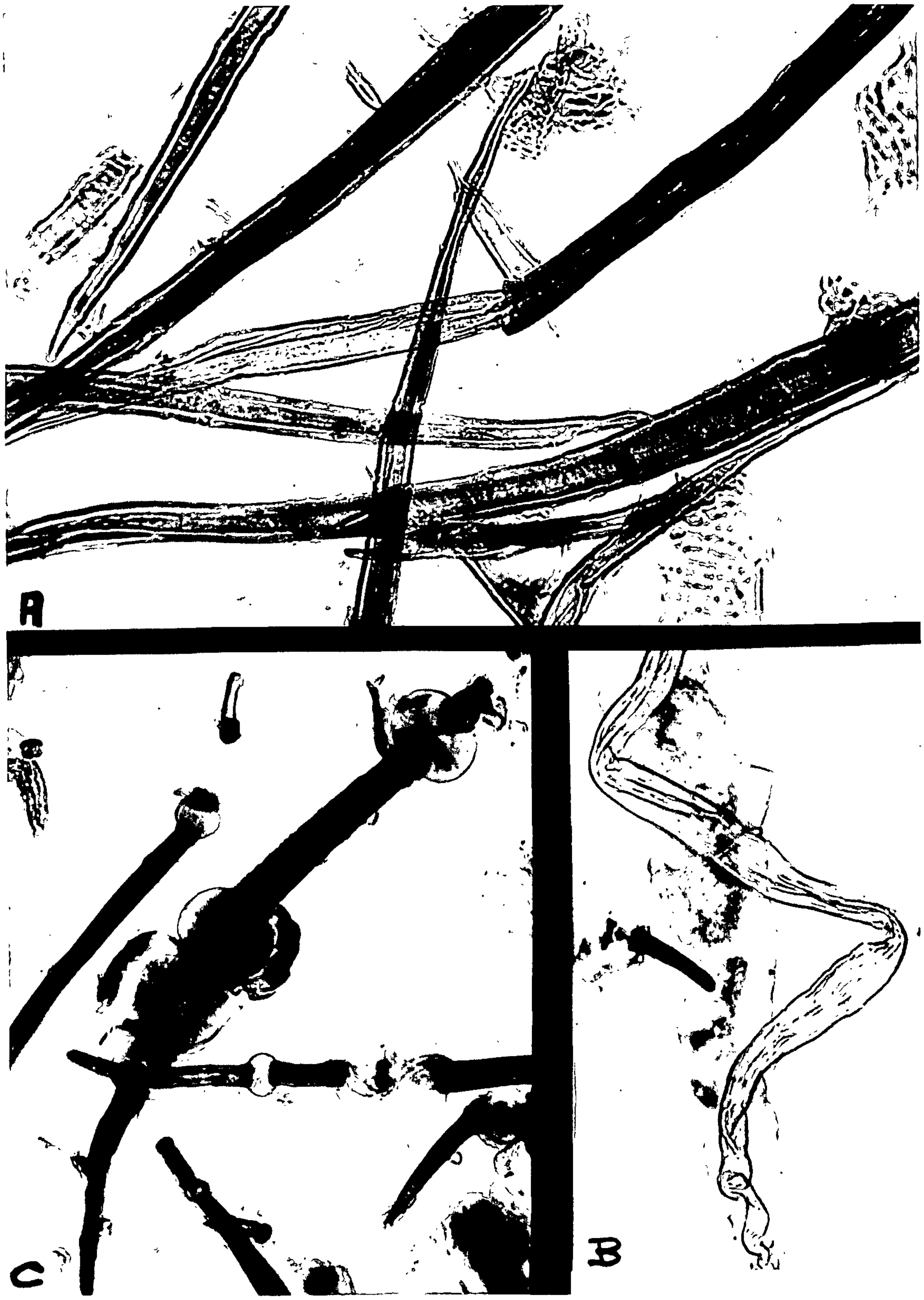

Figure 19. Bleached Fibers Obtained as Referred to in Table XXI, Showing Differences Between Fibers. (A) Victoria Blue Stain Mount; Magnification 365X. (B) and (C) Victoria Blue Stain and Cuprammonium Solution; Magnification 275X and 185X, Respectively

The fibers on the lower left-hand side of Fig. 19 were stained similar to the fiber just discussed, but exhibit the well-known ballooning effect caused swelling of the main secondary wall through weak points in the outer layer or la of the fiber. These outer parts then slide back along the fiber to form restr: bands. To form balloons, the outer layers must be sufficiently strong to resi: the internal pressure; otherwise the fiber will swell without forming balloons, in the example on the lower right. Through its blue color, which shows in Fig as black, the fiber positioned diagonally across the lower left-hand photograph still had the primary wall attached, whereas an intersecting fiber and one lyir about parallel both lack evidence of a primary wall. Presumably, the S_1 layer outer secondary wall is sufficiently strong in these to resist much of the inte swelling pressure. It is therefore concluded that the outer wall of a bleache pulp fiber may be too weak to resist the potential swelling pressure of the ma: secondary wall, or it may be able to withstand this pressure through the prese of relatively undamaged outer secondary wall to which the primary may still be attached. In other words, the bleached pulp fibers are apparently somewhat h geneous with respect to the outer wall.

Since one of the key features of pulping by selective delignificati with active chemicals is reducing chips in size to a degree sufficient to obt uniform chemical reaction, it is of particular interest to be able to obtain idea of whether size reduction causes excessive damage to the papermaking fib In Report Three, Fig. 9-14 and Table X gave some indication of there being a ponderance of whole fibers after chip fiberization, and from Fig. 1 of this r it appears chip fiberization was achieved with a loss of only about 5% in zer strength. Nevertheless, in view of the failure of previous workers to disc acceptable chemical pulping process based on the use of some form of fiberized chips, it is desirable not to overlook detection of possible shortcomings in the chip fiberization technique used in this work.

It is known, for example, that the compression of fibers in wood can cause losses as high as 50% in some strength properties of paper made from sulfite pulps (16). An undamaged sulfite pulp fiber swollen in cupriethylenediamine, for example, will remain in the characteristic balloon form for an indefinite period. On the other hand, a similar fiber from compression-damaged wood will swell and disperse without ballooning.

To consider the extent to which the fiber population in a selectively delignified pulp made from fiberized chips may have suffered loss in physical strength of the fiber walls, the upper part of Fig. 20 may be examined. This photograph was made after unbeaten, unbleached Pulp LL-60 had been stained with Victoria Blue and the fibers swollen in cuprammonium solution. It shows that for the same time of exposure to the swelling agent, some fibers have withstood swelling pressure, whereas other fibers have become swollen to the extent of almost being dispersed. This indicates there is not only appreciable between-fiber differences in outer wall structures but also some fibers have probably suffered compression damage to the detriment of their strength. Thus, there is reason to believe that through improved techniques in the mechanical aspects of the studies undertaken in this project, better fiber strength properties could be obtained.

Studies by a number of workers on the mechanical effects on fiber wall structure have included examination of holocellulose fibers. McIntosh, for example, has noted that when unrefined holocellulose fibers are swelled in cupriethylenediamine

Figure 20. Unbeaten, Unbleached Fibers of Pulp LL-60 Stained with Victoria Blue and Swollen in Cuprammonium Solution

the primary wall was generally released as a fairly intact sheath (17). This kind of phenomenon was observed when examining the unbeaten, unbleached Pulp LL-60 and is illustrated in the lower half of Fig. 20.

In the present approach used to prepare a pulp by selective delignification, the optimum situation would involve separation in the compound middle lamella region during chip fiberization. Thus, the question arises as to whether at some stage the primary wall will become detached from the fiber wall, create an excessive amount of fines in the pulp, and adversely affect drainage properties. In this connection, it is noted with interest that when holocellulose fibers were refined in a PFI mill at 10% consistency (17), although the primary wall was damaged, an appreciable amount remained on the fiber even when swollen in cupriethylenediamine.

Alkali Extraction and Surface Changes

In view of the importance of achieving separation into individual fibers, it seems appropriate to review briefly some studies carried out at The Institute of Paper Chemistry.

When wood is delignified, as in the preparation of holocellulose, if the simple concept of a fiber being surrounded with lignin is accepted, fiber in holocellulose would be expected to separate with ease. In practice, this does not happen.

That the above concept is an oversimplification of the real situation can be shown by consideration of Fig. 21 (18). Each of the photographs in this figure shows the radial face of the zone between two fibers of a holocellulose preparation. In all cases, the physical connection running vertically between two fibers is discernible, and after alkali extraction there is a noticeable change in the appearance of the fibers through more complete exposure of randomly oriented microfibrils.

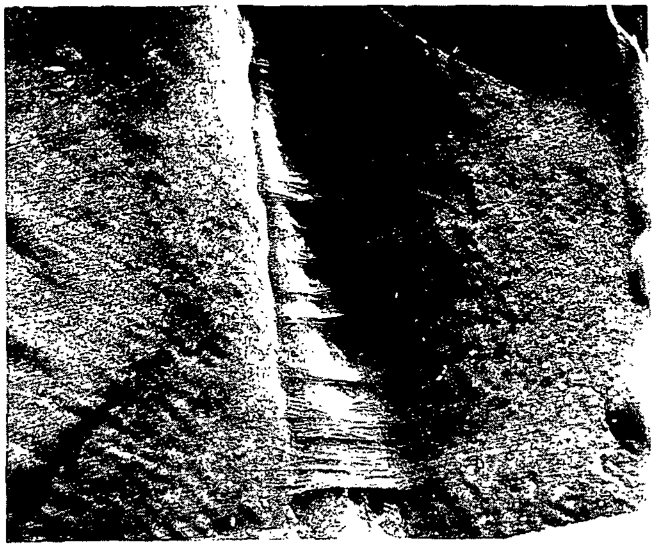

Plate A

Plate B

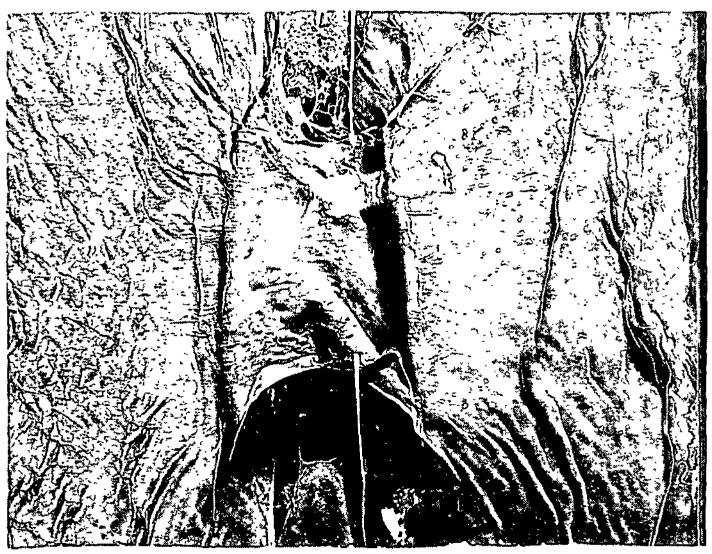

Plate C

Figure 21. Radial Faces of Interfiber Zone of Longleaf Pine Holocellulose; (A) After Freeze Drying, Magnification 6300X; (B) After Overnight Extraction with 0.1N KOH and Air Drying, Magnification 6300X; (C) After 10-Sec. Extraction with 0.1N KOH and Freeze Drying, Magnification 3200X [After Dunning (18)]

This is most clearly seen by comparing Plate A with Plate B. Extensive studies (18) have shown that in holocellulose there is little or no substance immediately behind the physical connection between fibers, as seen in Plate C.

One way to break the thin bridges and any other remaining bonds between fibers is by the application of mechanical force without the use of chemicals, as used to give an 80%-yield aspen pulp described in Report Three. In the present report, particular attention has been given to extraction with alkali, as already described, to weaken the interfiber structure after some reaction with chlorine dioxide and thereby achieve fiber separation. This procedure is thought of as simultaneously removing modified lignin and changing the nature of the fibers.

OXIDANT CONSUMPTION

DISCUSSION

Lignin Modification as a Function of Chlorine Dioxide Added

Although in this part of the project no practical work has been aimed at reducing the amount of chlorine dioxide used to below 9.0%, since the cost of oxidant is of key importance to the viability of a workable selective delignification pulping process, the present basis for believing significantly less chlorine dioxide could be needed under foreseeable circumstances will be considered.

In reviewing the work on the chemistry of hololignin by Buchanan, if lignin modification is considered as a function of chlorine dioxide that has been added and reacted with fiberized chips, some very interesting observations can be made. To discuss these, data derived from Report Four are presented in Table XXII.

From this it can be seen that when extracted fiberized aspen is reacted with progressively more chlorine dioxide, there is progressively less Klason plus acid-soluble lignin in the reacted fiberized aspen. In the spent liquor, there is also progressively more acetone-soluble material accounted for, but the three materials of this type have a remarkable similarity in chlorine and methoxyl content, acid numbers, and reactivity toward chlorine dioxide consumption under similar conditions. This appears to mean that irrespective of whether about 6, 9, or 18% chlorine dioxide is added, a substantial part of the lignin that is dissolved was degraded to about the same extent.

The three reacted fiberized aspen products when extracted with alkali gave residual reacted aspen with progressively less Klason plus acid-soluble lignin corresponding to reaction with progressively less chlorine dioxide. However, the total

TABLE XXII

CHEMISTRY OF HOLOLIGNIN[a]: DEGRADATION OF LIGNIN AND PRODUCT REACTIVITY TO ClO_2

	Extrd. Fiberized Aspen (95.8%[b]) — % ClO_2			Alkali Extraction[c] After — % ClO_2		
	5.75	8.6	17.2	5.75	8.6	17.2
	Reacted Fiberized Aspen[c]			Residual Reacted Aspen[c]		
Yield, %	92.2	90.3	81.7	75.8	69.0	69.0
Total lignin, %	20.9	18.5	11.1	8.9[d]	5.8[d]	3.7[d]
Klason, %	15.7	12.6	5.9	7.4(i)	4.4(i)	2.6(i)
Acid sol., %	5.2	5.9	5.2	1.5(ii)	1.4(ii)	1.1(ii)
Total mod. lig., % (i + ii + iii)	18.2	19.6	14.4	--	--	--
Chlorine, % (total lig. basis)	3.1	3.9	7.4	1.7	2.4	3.7
	Spent Liquor[c]			Alkali Extract		
Total org. solids, % (possible)	4.4(3.6)	6.0(5.5)	6.2(14.1)	(16.4)	(21.3)	(12.7)
Acetone sol., %	1.7	3.1	4.8	9.3(iii)	13.8(iii)	10.7(iii)
% Chlorine, based on above	18.5	16.5	17.6	3.6	5.0	6.2
% Methoxyl, ditto	6.1	4.3	4.3	15.4	15.3	10.5
Acid no. I, ditto[e]	8.5	9.0	7.6	3.8	3.9	5.1
Acid no. II, ditto	26.4	27.8	26.8	11.4	10.1	15.8
% ClO_2 consumption, ditto	22	25	17	65	65	61
90% Acetone sol., %	0.3	0.5	0.6	5.9	3.4	0.9

[a] Project 2500, Report Four, M. A. Buchanan, January 16, 1968.

[b] Yield, after extraction with acetone, expressed on an o.d. fiberized chip basis. Extracted aspen had 21.8% Klason and 2.0% acid-soluble lignin.

[c] See Fig. 5 as under note a.

[d] Hence lignin removed was 2.59, 2.01, and 1.17 g./g. ClO_2 for the addition of 5.75, 8.6, and 17.2% aqueous ClO_2.

[e] Acid no. I is based on g. KOH/100-g. sample to the first inflection point, and acid no. II to between the first and second inflection points, Report Four.

lignin for each product had been significantly reduced by alkali extraction. This is the purpose of following the reaction between fiberized chips and oxidant with an alkali extraction. In concept, the aim is to modify the lignin only enough to impart solubility in alkali, and consideration of the data on the alkali extract reveals something about how much modification is enough. If the methoxyl content, acid numbers, and reactivity toward chlorine dioxide of the acetone-soluble materials are compared, the similarity is striking. This appears to mean that irrespective of whether about 6, 9, or 18% chlorine dioxide is added, the acetone-soluble portion of the modified lignin dissolved in alkali was degraded roughly to the same degree. Furthermore, the extent of this degradation is not only significantly less than for the acetone-soluble materials in the spent liquor, but also sufficiently restricted so that reactivity toward chlorine dioxide is at least twice that of the degraded products in the spent liquors. If the data on the acetone-soluble materials in the alkali extract are examined more closely, it will be seen from the chlorine analyses that there is progressively less chlorine present for less chlorine dioxide added. In addition, the residual reacted aspen materials have a similar drop in bound chlorine. It appears that there is a greater degree of chlorine substitution, at least some of which is unnecessary, when progressively more chlorine dioxide is added.

Expectation of Reducing Chlorine Dioxide Requirement

Since chlorine substitution occurs when lignin is removed by degradation with chlorine dioxide and alkali extraction, it is possible a significant portion of the chlorine dioxide added could be replaced by a significant amount of chlorine. Preliminary work along these lines is now in hand.

From the data in Table XXII, there is also some reason to expect the chlorine dioxide needed could be reduced below 9.0%, irrespective of chlorine addition. In a footnote to Table XXII, it is recorded that about 2.6, 2.0, and 1.2 g. lignin were removed per g. chlorine dioxide for the addition of 5.76, 8.6, and 17.2% aqueous chlorine dioxide, respectively. Since the nature of the modified lignin products seems to be roughly independent of the amount of chlorine dioxide added, it can be argued that if optimum conditions existed, it is conceivable the chlorine dioxide needed could be reduced to $\frac{2.0}{2.6}$ of 9.0, or 7.0%. This not only implies lignin would be modified just enough to become soluble in alkali, but also implies the fiberized aspen is not yet in an ideal form in terms of fiber bundle size with respect to process reactions. Some support for this contention was obtained by the observation that 3% of partially modified lignin was dissolved when chlorine dioxide-reacted fiberized chips were further separated in a PFI mill.

While these considerations for reducing oxidant consumption involve some speculation, they do at least provide a basis for believing significant reduction of the chlorine dioxide requirement is a real possibility.

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